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ON DEHYDROMUCIC ACID.

BY HENRY B. HILL.

Although dehydromucic acid was first described twenty-five years ago, and already has been made the subject of a number of investigations, a more extended study of it promised to yield interesting results. The chief obstacle to such a study lay in the difficulty of preparing larger quantities of the acid. It was first obtained by Fittig and Heinzelmann,[1] in 1876, by the action of fuming hydrobromic acid under pressure upon mucic acid. The method subsequently given by Heinzelmann,[2] in 1878, was to heat mucic acid for two days in a sealed tube, at 100°, with hydrobromic acid saturated at 0°. The dehydromucic acid which was formed was then separated from the unaltered mucic acid by means of its more readily soluble barium salt. In the following year Seelig[3] found that concentrated hydrochloric acid could be substituted for the hydrobromic acid, and in 1882 Klinkhardt[4] felt justified in recommending a mixture of the two acids as most advantageous. In 1888 Sohst and Tollens[5] found that acid potassic saccha-

[1] Ber. d. chem. Ges., 9, 1198.
[2] Ann. Chem. (Liebig), 193, 184.
[3] Ber. d. chem. Ges., 12, 1083.
[4] J. prakt. Chem., [2], 25, 41.
[5] Ann. Chem. (Liebig), 245, 19.

rate gave 27.5 per cent of its weight of pure dehydromucic acid when heated for three hours at 150° in a sealed tube with concentrated hydrochloric acid; they also found that a high melting acid was slowly formed by the action of boiling concentrated hydrochloric acid under ordinary pressure. A little later Schrötter[1] showed that dehydromucic acid was formed under these conditions, but that the reaction ran so slowly that after nine days' heating with 30 per cent hydrochloric acid under return condenser a yield of only 16 or 18 per cent of the weight of the potassic saccharate taken could be obtained. Although the method of Schrötter made it possible to prepare larger quantities of the acid in one operation, the long boiling and the comparatively small yield left much to be desired.

In attempting to find a more convenient method of preparation many experiments, which need not be described in detail, were made upon mucic acid and its esters with a variety of dehydrating agents. Although small quantities of dehydromucic acid were in most cases formed, no profitable method for its preparation was found. Our attention was then attracted by the statement of Schmidt and Cobenzl[2] that potassic dehydromucate was formed by the dehydration of neutral potassic mucate at high temperature in a stream of hydrogen. They seem, however, to have made no attempt to identify the salt which they analyzed, or to prepare from it dehydromucic acid. Dr. I. K. Phelps was unable to prepare a neutral potassic mucate containing 2 molecules of water of crystallization, which Schmidt and Cobenzl assert that they used in their experiment, and found that the ordinary anhydrous salt lost in weight very slowly at 200°, while deep-seated decomposition had evidently set in at this temperature. Moreover, it was found that potassic dehydromucate possessed properties entirely different from those which were ascribed by Schmidt and Cobenzl to the salt in question.

We therefore returned to the action of haloid acids and found that boiling concentrated hydrobromic acid at ordinary pressures effected a tolerably rapid conversion of mucic into

[1] Sitzungsber. kk. Acad. Wien, 97, 2b, 407.
[2] Ber. d. chem. Ges., 17, 599.

dehydromucic acid. With saccharic acid, which in the form of its acid potassium salt is even more readily accessible, the reaction ran more rapidly, and after boiling for sixteen hours under return condenser a nearly colorless dehydromucic acid could readily be obtained, which amounted to 25 or 30 per cent of the weight of the saccharate taken. Subsequent experiments showed that this yield could materially be increased by taking a somewhat stronger hydrobromic acid in quantity sufficient to leave a distillable acid after the formation of the potassic bromide.

Dr. I. K. Phelps and Mr. W. J. Hale then studied dehydromucic acid, and prepared certain of its derivatives. Klinkhardt[1] had already established the extreme indifference of the acid toward anhydrous bromine; further experiments in this direction showed that dehydromucyl chloride was as refractory as the acid itself. No evidence of substitution was obtained on heating the chloride with bromine under the most varied conditions. With aqueous bromine a reaction was noticed analogous to that observed by Hill and Sanger[2] with δ-brompyromucic acid, and afterwards studied by Hill and Hartshorn.[3] The decomposition was most complete in alkaline solution, and yielded then dibromfurfuran tetrabromide and carbonic dioxide. By the action of bromine upon the potassium salt of the acid ethyl ester δ-pyromucic acid was apparently formed. By the action of aluminic chloride upon a solution of the acid chloride in benzol the corresponding diphenyl ketone was readily made. No satisfactory products could be obtained by the reduction of this ketone; it yielded, on oxidation, as might have been expected, derivatives of benzoic and maleic acids.

More interest attached to the acids formed by the reduction of dehydromucic acid, and their study was undertaken by Mr. A. S. Wheeler.

In 1876 Fittig and Heinzelmann[4] had found that dehydromucic acid was converted into a more readily soluble acid, which melted at about 140°, by the action of sodium amalgam,

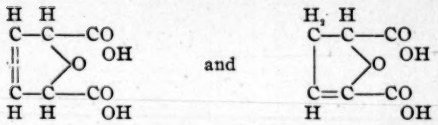
[1] J. prakt. Chem., [2], **38**, 50.
[2] Proc. Am. Acad., **21**, 145; Ann. Chem. (Liebig), **232**, 55.
[3] Ber. d. chem. Ges., **18**, 448.
[4] *Ibid.*, **9**, 1199.

and three years later Seelig[1] showed, in Fittig's laboratory, that two isomeric acids with the formula $C_6H_8O_5$ could be isolated from the product of this reduction, and that they could be separated through the difference in solubility of their barium salts; Seelig distinguished these two products, which melted at 146° and the second at 173°, as the "hard" and "soft" acids, while Beilstein designated them as the α- and β-acids, respectively. Seelig's description of his results is not always readily intelligible, but his experimental work was evidently done with care and we have been able to confirm substantially all his results. In 1888 Schrötter[2] again studied the reduction of dehydromucic acid and came to the conclusion that the α-acid was the only product of the reaction. While Schrötter is doubtless correct in asserting that the α-acid is the only direct product of the reduction, we have not found it possible to avoid the partial isomerization of this acid, and our product has therefore always contained more or less of the higher melting β-isomer. The quantity of this higher melting acid is very small, if the reduction is carried on at 0°, and the sodic hydrate which is formed is neutralized by a rapid stream of carbonic dioxide; on the other hand it becomes the main product, if the reaction is carried on at ordinary temperature and the sodic hydrate is allowed to accumulate. The isomerization of the pure α-acid is also rapidly effected by warming its alkaline solution. If a strongly alkaline solution of the β-acid is boiled for a long time, a new isomeric acid is formed in quantity.

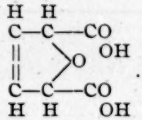
This γ-acid shows no sharp melting-point, but decomposes at 190°–200°, according to the rate at which it is heated. While the α- and β-acids cannot be further reduced by sodium amalgam, the γ-acid readily takes two additional atoms of hydrogen and forms the tetrahydrofurfuran dicarboxylic acid, which has recently been described by Lean.[3]

Two structurally isomeric acids can evidently be formed by the addition of two atoms of hydrogen to dehydromucic acid:

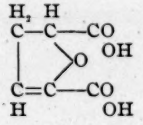
[1] Ber. d. chem. Ges., **12**, 1085.
[2] Sitzungsber. kk. Akad. Wien, **97**, 2*b*, 409
[3] J. Chem. Soc., **77**, 103.



The first of these contains two asymmetric carbon atoms and should give an inactive (cis) form and two optically active (cis-trans) forms. The second formula, with its single asymmetric carbon, gives the possibility of two stereometrically different active modifications and their racemic combination. Our investigation has shown that the α-dihydrofurfuran-αα'-dicarboxylic acid is the cis form of the first structure, the β-acid is the inactive combination of the two active cis-trans forms, while the γ-acid has the second structure formula and is made up of the two possible active bodies. The position of the double bond in the three dihydrofurfuran dicarboxylic acids is sufficiently indicated by the methods of their formation. The α-acid as the first product of the reduction of dehydromucic acid must have the formula

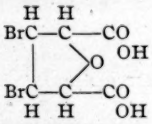


The β-acid probably has the same structure since it is unstable in alkaline solution, while the γ-acid, which is the final product formed by the action of alkalies, undoubtedly has the form



These conclusions are warranted by the facts established by v. Baeyer and his pupils in their study of the analogous reduction of the aromatic acids, and they are confirmed by

the behavior of the acids in question. By the prolonged action of sodium amalgam the γ-acid is converted into the corresponding tetrahydrofurfuran dicarboxylic acid, while the α- and β-acids cannot be further reduced; in the case of analogous acids it is established that hydrogen is added to doubly tied carbon atoms under these conditions only when the double bond is adjacent to a carboxyl. Oxidizing agents gave no decisive indication of differences in structure; the chief products in each case were dehydromucic and oxalic acids, although it was noticeable that the α-acid gave the largest yield of dehydromucic acid and the γ-acid gave the smallest. The acids in question readily add bromine, forming products to which the formulæ



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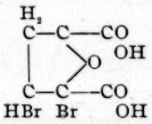
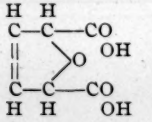


must be assigned.

The α- and β-dibromides are decomposed in alkaline solution in the cold with the elimination of carbonic dioxide and the almost quantitative formation of pyromucic acid; the γ-dibromide also loses carbonic dioxide in alkaline solution, but no pyromucic acid is formed. This reaction leaves no doubt that the α- and β-acids and their dibromides have the identical structures:



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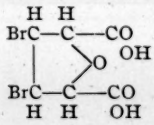


Since the α- and β-acids were both optically inactive it followed that one of them should be separable into two antipodal active modifications. This conclusion was reached only toward the close of our investigation and we have been able to make but few preliminary experiments in this direction. We have found that the β-acid gives two cinchonine salts of

widely different solubility, and that the acids prepared from these salts are optically active with opposite rotations to approximately the same amount. We have not yet prepared the two forms in a pure condition, and must reserve for the future a careful study of the active forms. Our preliminary experiments have also shown us that the γ-acid can be separated into two optically active components.

CXXI.—On Dehydromucic Acid and Certain of Its Derivatives.

By Isaac K. Phelps and William J. Hale.

In the course of an extended series of experiments upon the dehydration of mucic acid and its esters it was found that dehydromucic acid was formed on boiling mucic acid with concentrated hydrobromic acid, under a return condenser, and that the formation was sufficiently rapid to serve as a convenient method of preparation. Subsequent experiments showed that the reaction ran much more quickly and completely with saccharic acid, and that the substitution of hydrobromic acid for the 30 per cent hydrochloric acid recommended by Schrötter for this purpose reduced the time necessary to complete the reaction from nine days to sixteen hours, while the yield of dehydromucic acid was very nearly doubled. In the preparation of acid potassic saccharate we have followed the method recommended by Sohst and Tollens.[1] Since the purification of large quantities of the salt by recrystallization is somewhat tedious on account of its slow deposition from solution, we have found it advantageous in the preparation of dehydromucic acid on a large scale to use the crude salt well washed with cold water and freed from the dark-brown mother-liquor by pressure. The saving in time and labor were apparently more than sufficient to compensate us for the diminished yield. At first a distilled hydrobromic acid (sp. gr. 1.49) was used, but later it was found that a stronger acid (sp. gr. 1.56) gave a larger yield; a crude acid made by the alternate addition of bromine and red phosphorus to water could be also used, but the weight of product obtained was then slightly diminished.

[1] Ann. Chem. (Liebig), **245**, 3.

The acid potassic saccharate is dissolved in from four to five times its weight of hydrobromic acid, and the solution heated to boiling under a return condenser. Oily drops soon appear in the cooler, carbonic dioxide is given off, and before long the separation of a dark-colored insoluble product begins. The length of time required to complete the reaction varies with the strength of the hydrobromic acid employed; if concentrated acid is used in quantity sufficient to leave an acid saturated at the boiling temperature after the liberation of the saccharic acid from its salt, the decomposition is found already completed at the end of sixteen hours; when distillable hydrobromic acid is used at the outset, the reaction is so nearly finished in this time that longer boiling gives but an insignificant additional product. The dehydromucic acid formed apparently separates completely from the concentrated hydrobromic acid on cooling. Direct experiment showed that distillable acid dissolved at ordinary temperatures about 0.01 per cent of its weight of pure dehydromucic acid, or 15 milligrams to 100 cc. From the black product of the reaction the acid may be extracted by the cautious addition of sodic carbonate, but as a slight excess of the carbonate dissolves also a large amount of coloring-matter, it is much better to make use of the calcium salt. Calcic dehydromucate is much more readily soluble than the barium salt, and on boiling the crude product with water and calcic carbonate, or even with calcic hydrate in excess, little coloring-matter is extracted. The light straw-yellow solution which is obtained yields, on acidification, a slightly colored acid which is sufficiently pure for all ordinary purposes. It may easily be purified by decolorizing with bone-black the solution of its calcium salt.

A number of experiments were made to determine the percentage of dehydromucic acid formed from acid potassic saccharate under different conditions. In each case the crude product was ground up with an excess of calcic carbonate, the mixture boiled with a large amount of water, and the insoluble residue thoroughly extracted with boiling water. The acid was then precipitated from the concentrated solution by the addition of hydrochloric acid and filtered off after standing over night. No correction was made for the solubility of

the dehydromucic acid in water; the volume of the mother-liquor and wash-water did not differ widely in the different cases, and it was not easy to determine how far the solubility was modified by the presence of calcic chloride and hydrochloric acid.

The purity of the acid potassic saccharate which was used is shown by the following analyses of two different preparations.

I. 0.5149 gram salt gave 0.1807 gram K_2SO_4.

II. 0.5558 gram salt gave 0.1942 gram K_2SO_4.

	Calculated for $C_6H_9O_8K$.	Found. I.	II.
K	15.77	15.75	15.69

The results of five successive experiments with this pure saccharate are given below. In each case 40 grams of the salt were taken, and the action of the boiling hydrobromic acid continued for sixteen hours. In I. and II. an acid of about 50 per cent was used, which was obtained by the action of red phosphorus upon bromine and water without distillation. In III. a distilled acid of about the same strength was employed. In IV. the same acid was used as in III., but the solution was concentrated by distillation until the boiling-point reached 125° and the original volume of the solution then restored by the addition of fresh distillable acid before boiling with return cooler. In each of these four cases 180 grams of hydrobromic acid were used. In the last case (V.) 195 grams of an acid of sp. gr. 1.565 were taken; on heating, a very small amount of hydrobromic acid escaped through the cooler.

	Weight dehydromucic acid.	Per cent yield.
I.	11.35	28.4
II.	11.50	28.8
III.	11.63	29.1
IV.	13.28	33.2
V.	13.85	34.6

It seemed of interest to make a careful determination of the percentage of dehydromucic acid which could be formed from mucic acid under similar conditions. Accordingly, 30 grams

of mucic acid were boiled with 130 grams of distillable hydrobromic acid under return condenser for sixteen hours. The insoluble product was then treated with calcic hydrate and water, and the dehydromucic acid precipitated from the filtered solution. The acid thus thrown down weighed but 6.05 grams, or 20.2 per cent of the mucic acid taken, and in the insoluble lime salt could be found unaltered mucic acid in abundance. It was not possible to determine with precision the amount of mucic acid which had escaped decomposition, but 11.30 grams of ammonic mucate, corresponding to 9.73 grams of mucic acid, were recovered. As a maximum, therefore, but 67.6 per cent of the mucic acid had been decomposed under conditions which apparently bring about the complete decomposition of saccharic acid, while the dehydromucic acid formed amounted to at least 29.9 per cent of the mucic acid which actually entered into reaction. As the mucic acid dissolves quite freely in the boiling hydrobromic acid this slow decomposition can hardly be due to the difference in solubility, but is probably connected with its configuration.

While it would not be profitable to give any account of our many unsuccessful attempts to prepare dehydromucic acid, it seems advisable to describe in some detail certain experiments with potassic mucate, which we were led to undertake by the statement of Schmidt and Cobenzl[1] that potassic dehydromucate could be made by the dehydration of potassic mucate at high temperature in an atmosphere of hydrogen. They analyzed the air-dried mucate which they used and found it to contain a percentage of potassium corresponding to the formula $K_2C_6H_8O_8.2H_2O$, but they make no mention of the previous work of Trommsdorff[2] or Hagen,[3] who found a much higher percentage of potassium in the salt, and they give no description of their method of preparation.

We prepared potassic mucate by the addition of potassic carbonate in slight excess to mucic acid suspended in boiling water. The salt deposited as the solution cooled (I.) or recrystallized from hot water (II.), when air-dried, proved to

[1] Ber. d. chem. Ges., **17**, 599.
[2] Gmelin's Handbuch, **5**, 878.
[3] Abhandlung, etc., Berlin, 1849. 5; Gmelin: *Ibid.*

contain an insignificant amount of water, and essentially the percentage of potassium required by the anhydrous salt. The slight deficit in potassium and the small percentage of water suggested the possible presence of a small amount of the acid salt, which crystallizes with 1 molecule of water. A new preparation was therefore made in precisely the same way except that potassic hydrate was added in considerable excess instead of the carbonate. The salt thus obtained, when well washed with cold water and dried by exposure to the air (III.), gave substantially the same result. The salt obtained by spontaneous evaporation at ordinary temperatures (IV.), or by the precipitation of a cold aqueous solution by the addition of alcohol (V.), also proved to be anhydrous. Finally, a cold saturated solution was partially frozen and the salt which separated with the ice was collected and dried at as low a temperature as we could conveniently command (10° to 12°), but the composition of the salt (VI.) was the same.

I. 0.3788 gram salt gave 0.2278 gram K_2SO_4; 1.8155 grams of the same salt lost, at 145°, 0.0025 gram H_2O.

II. 0.5000 gram salt gave 0.3015 gram K_2SO_4.

III. 0.3854 gram salt gave 0.2331 gram K_2SO_4.

IV. 0.3846 gram salt gave 0.2327 gram K_2SO_4; 1.4744 grams of the same salt lost, at 145°, 0.0021 gram H_2O.

V. 1.2629 grams salt lost, at 145°, 0.0037 gram H_2O.

VI. 0.3889 gram salt lost, at 145°, 0.0009 gram H_2O; and gave 0.2336 gram K_2SO_4.

	Calculated for		Found.					
	$K_2C_6H_6O_6$.	$K_2C_6H_6O_6.2H_2O$.	I.	II.	III.	IV.	V.	VI.
K	27.34	24.29	27.00	27.07	27.15	27.16	....	26.98
H_2O	....	11.18	0.14	....	....	0.14	0.29	0.23

Although we had not succeeded in preparing a neutral potassic mucate which had the composition assigned to it by Schmidt and Cobenzl, there seemed to be no doubt that the ordinary anhydrous salt could be used equally well for the complete dehydration which they describe, since the hydrous salt must lose its water of crystallization long before any more essential alteration could take place. We therefore heated this salt, contained in a small flask immersed in an oil-bath, in a current of dry hydrogen free from carbonic dioxide; the

water and carbonic dioxide formed were then collected in weighed absorption tubes. While Schmidt and Cobenzl found that dehydration was complete at 200°, and that the salt then remained practically unaltered at 240°, we found that the loss of weight below 200° was insignificant, and even at 205° to 210° that water was given off but slowly.

4.5352 grams air-dried salt, when heated for twenty-three hours at 150° to 210°, gave 0.0248 gram CO_2 and 0.1039 gram H_2O.

	Calculated for $K_2C_6H_6O_6$.	Found.
$3H_2O$	18.87	2.29
CO_2	....	0.55

As the dehydration was proceeding so slowly, and deep-seated decomposition had evidently already set in, the heating was discontinued. It seemed best, however, to examine the residual salt carefully for dehydromucic acid, which might possibly have been formed in small quantity. Schmidt and Cobenzl had extracted their dehydrated salt with hot water to remove unaltered potassic mucate, and had recrystallized from boiling water the sparingly soluble residue. On cooling they obtained beautiful white scales, which contained the percentage of potassium required by potassic dehydromucate; but they seem to have made no attempt at a further identification of the salt. On the other hand, our own experiments, which will soon be described, had shown that potassic dehydromucate crystallized in long needles, which were soluble in less than twice their weight of cold water. We therefore examined separately the portions of the heated salt which were most readily and most sparingly soluble in water. Cold water gave an almost black solution, which deposited a dark-colored, flocculent precipitate on acidification. This precipitate was heated with calcic hydrate and water, the solution filtered and evaporated to a small volume; on acidification no dehydromucic acid was deposited. The salt was then extracted with hot water until the greater part had gone into solution. As the residue still appeared to be potassic mucate, it was acidified with hydrochloric acid and the acid obtained treated with calcic hydrate as before; but in this case also the acidified solu-

tion remained perfectly clear. When 0.01 gram of dehydromucic acid was mixed with 1 gram of mucic acid and the mixture was treated in the same way with calcic hydrate, enough dehydromucic acid could easily be recovered to identify it by means of its characteristic reaction with ferric chloride. We must conclude, therefore, that no sensible amount of dehydromucic acid had been formed from potassic mucate after heating for twenty-three hours; for seventeen hours the temperature had been held at 200° to 210°.

Potassic Dehydromucate, $K_2C_6H_4O_5.H_2O$.—As this salt had not previously been described it was prepared by adding potassic carbonate in slight excess to dehydromucic acid suspended in a little water. The concentrated solution gradually solidifies with the separation of slender prisms, but the salt may be obtained more conveniently by the addition of alcohol to the aqueous solution. From hot 75 per cent alcohol it crystallizes in long silky needles, which dissolve in less than twice their weight of cold water.

I. 0.3498 gram of the air-dried salt gave 0.2439 gram K_2SO_4.

II. 2.0986 grams air-dried salt lost at 200° 0.1483 gram H_2O.

	Calculated for $K_2C_6H_2O_5.H_2O$.	Found. I.	II.
K	31.28	31.30	....
H_2O	7.20	....	7.07

Determinations of the solubility of the acid and its barium salt, which we owe to Mr. A. S. Wheeler, may best find place here; we add our own determination of the solubility of the calcium salt.

Dehydromucic Acid.—The saturated solution of the acid was boiled with baric carbonate, and the barium precipitated with sulphuric acid from the filtered solution.

I. 45.95 grams solution, saturated at 18°, gave 0.0693 gram $BaSO_4$.

II. 48.65 grams solution, saturated at 18°, gave 0.0722 gram $BaSO_4$.

According to these determinations the solution saturated at 18° contained the following percentages of the acid:

I.	II.
0.101	0.099

Baric Dehydromucate.—The barium was determined by precipitation.

I. 43.79 grams solution, saturated at 18°, gave 0.3190 gram $BaSO_4$.

II. 42.96 grams solution, saturated at 18°, gave 0.3127 gram $BaSO_4$.

The solution saturated at 18° therefore contained the following percentages of the anhydrous salt:

I.	II.
0.91	0.91

Calcic Dehydromucate.—The calcium in the saturated solution was determined by evaporation with sulphuric acid.

I. 9.347 grams solution, saturated at 18°, gave 0.2576 gram $CaSO_4$.

II. 9.573 grams solution, saturated at 18°, gave 0.2647 gram $CaSO_4$.

The aqueous solution saturated at 18° therefore contains the following percentages of the anhydrous salt.

I.	II.
3.93	3.94

This solubility is approximately doubled by heating the solution to boiling.

Monomethyl Dehydromucate, $C_7H_8O_5$.—This body was made by allowing 1 molecule of potassic hydrate to act upon dimethyl dehydromucate[1] dissolved in methyl alcohol. At ordinary temperature the alkaline reaction gradually disappears and the acid ester may then be precipitated from the concentrated solution by the addition of hydrochloric acid. It may easily be purified by recrystallization from hot water.

0.1346 gram substance gave 0.2442 gram CO_2 and 0.0446 gram H_2O.

	Calculated for $C_7H_8O_5$.	Found.
C	49.42	49.50
H	3.56	3.71

[1] Zenoni (Gazz. chim. ital., **20**, 519) gives the melting-point of the dimethyl ester as 112°. After repeated recrystallization, or sublimation, we have found the melting-point constant at 109° to 110° (corr.).

The monomethyl dehydromucate is readily soluble in alcohol or ether, sparingly soluble in chloroform, and insoluble in benzol or ligroin. It dissolves freely in hot water, and as the solution cools is deposited in lustrous leaflets which melt at 201° to 202° (corr.).

Monoethyl Dehydromucate, $C_8H_8O_6$.—The diethyl ester was allowed to stand in alcoholic solution with 1 molecule of potassic hydrate until the alkaline reaction had disappeared. The alcohol was then expelled by heat with the addition of water, the aqueous solution filtered and acidified. The product thus obtained was recrystallized from hot water.

0.2200 gram substance gave 0.4216 gram CO_2 and 0.0898 gram H_2O.

	Calculated for $C_8H_8O_6$.	Found.
C	52.16	52.28
H	4.38	4.57

The monoethyl dehydromucate is readily soluble in alcohol, more sparingly soluble in ether, sparingly soluble in chloroform or benzol, and insoluble in ligroin. It is readily soluble in hot water and separates, as the solution cools, in clustered needles which melt at 148° to 149° (corr.).

Dehydromucic Acid Amide, $C_6H_5NO_4$.—Ammonic hydrate in concentrated solution readily converts the acid ethyl ester into the corresponding amide, and the reaction is completed at ordinary temperatures in the course of twenty-four hours. The acid amide is insoluble in the ordinary organic solvents, but crystallizes well from hot water in the form of long slender needles, which melt at 280° to 281° (corr.).

0.2246 gram substance gave 17.8 cc. moist nitrogen at 21°.5 and under a pressure of 774 mm.

	Calculated for $C_6H_5NO_4$.	Found.
N	9.06	9.13

Dehydromucic Dianilide, $C_6H_4O_2(NHC_6H_5)_2$.—A slight excess of aniline was added to dehydromucyl chloride dissolved in eight times its weight of ether, and the product, which was at once formed, was crystallized from 50 per cent alcohol after washing well with water; it crystallizes in long, radiating

needles, which melt at 227° to 228° (corr.). The body is practically insoluble in ether, ligroin, or boiling water; it is very sparingly soluble in benzol, somewhat more readily soluble in chloroform, but readily soluble in alcohol.

0.1606 gram substance gave 12.8 cc. moist nitrogen at 20°.5 and under a pressure of 770 mm.

	Calculated for $C_{18}H_{14}N_2O_8$.	Found.
N	9.18	9.18

Dehydromucicdiacetic Anhydride, $C_{10}H_8O_7$.—When dehydromucic acid is heated under return condenser with an excess of acetic anhydride[1] it gradually goes into solution, and on cooling colorless leaflets of the mixed anhydride are deposited. The body may be recrystallized from hot acetone or benzol. It is sparingly soluble in ether or ligroin, more readily soluble in boiling benzol, acetone, ethyl acetate, glacial acetic acid, or chloroform. The melting-point of the substance could not be determined since it is rapidly decomposed at about 150° with the formation of acetic anhydride.

0.1634 gram substance gave 0.2988 gram CO_2 and 0.0500 gram H_2O.

	Calculated for $C_{10}H_8O_7$.	Found.
C	49.99	49.87
H	3.36	3.42

The molecular weight of the substance was determined by means of the boiling-point of the solution in benzol with the following results:

Substance.	Solution.	Elevation.	Molecular weight.
0.1312	18.85	0.075	247.8
0.1196	18.75	0.068	250.5
0.1500	18.65	0.087	246.8

Dehydromucic Anhydride, $C_{12}H_4O_5$(?).—By the rapid heating of dehydromucic acid with phosphoric pentachloride Klinkhardt[2] obtained an amorphous, sublimable body, soluble in alcohol, which he thought might possibly be the anhydride of the acid, but he did not examine the substance more

[1] Schrötter states (*Loc. cit.*, 410) that acetic anhydride has no action upon dehydromucic acid.

[2] J. prakt. Chem., [2], **23**, 46.

carefully. On repeating the experiments of Klinkhardt we have not succeeded in isolating any definite product except the chloride of the acid. On heating this acid chloride with 1 molecule of the acid or of its salts, we obtained no satisfactory results, and Klinkhardt had already found that dehydromucic acid was converted into its chloranhydride when it was heated with acetyl chloride. When the diacetic anhydride which has just been described was heated to 150° most conveniently under diminished pressure, we found that decomposition took place, that acetic anhydride distilled off, and that the pale-yellow residue which remained had the composition required by dehydromucic anhydride. The substance proved to be practically insoluble in all ordinary solvents, and by heat it was decomposed without melting. Under diminished pressure the slow formation of a crystalline sublimate was noticed at high temperature, but purification by sublimation appeared to be impracticable. The substance was therefore extracted successively with boiling acetic anhydride and acetone, and analyzed with no attempt at further purification.

I. 0.1730 gram substance gave 0.3298 gram CO_2 and 0.0292 gram H_2O.

II. 0.1800 gram substance gave 0.3420 gram CO_2 and 0.0276 gram H_2O.

	Calculated for $C_6H_2O_4$.	Found. I.	II.
C	52.17	52.01	51.82
H	1.46	1.89	1.71

The dehydromucic anhydride was very slowly attacked by boiling water, but hot caustic alkalies soon carried it into solution. The physical properties of the body were such that its molecular weight could not be determined directly; it seems probable, however, that it is formed from 2 molecules of the acid.

Action of Halogens.

The behavior of dehydromucic acid towards dry bromine was investigated by Klinkhardt, who found that no addition-product could be formed, and that no substitution took place when the acid was heated with bromine. It seemed advisable to

make further experiments in this direction under conditions which are ordinarily more favorable to the formation of substitution-products. The acid chloride melting at 80° was accordingly heated with bromine, in a sealed tube, to 250°, but no hydrobromic acid was formed and no change was apparent. On heating the mixture in direct sunlight, or with the addition of bromides of aluminium or phosphorus under varied conditions, we were equally unsuccessful.

Klinkhardt had already shown that fumaric acid is formed by the action of aqueous bromine, but we were interested to know whether, under favorable conditions, substituted furfurans could not be formed as Hill and Sanger[1] had shown to be the case with δ-brompyromucic acid. Four molecules of bromine were therefore added to an aqueous solution of potassic dehydromucate and the product which separated on standing collected by extraction with ether. The product was partially soluble in hot ligroin, and as the solution cooled dibromfurfurantetrabromide separated, which melted at 111° after several recrystallizations from ligroin. The portion of the product which was insoluble in ligroin was recrystallized from hot water, and recognized from its crystalline form and its behavior in capillary tube as ordinary dibromsuccinic acid. The formation of the dibromsuccinic acid could almost entirely be avoided by the addition of an excess of potassic carbonate to the dilute solution of the dehydromucate and then adding the bromine slowly with constant shaking. From 2 grams of dehydromucic acid 3 grams of dibromfurfurantetrabromide were then obtained. After several recrystallizations from ligroin it melted at 112° and gave, with alcoholic potassic hydrate, the tetrabromfurfuran melting at 65°.

0.1096 gram substance gave 0.2266 gram AgBr.

	Calculated for $C_4H_2Br_4O$.	Found.
Br	87.90	87.98

Iodine also reacts upon potassic dehydromucate with the formation of diiodfurfuran, but the reaction takes place promptly only at temperatures above 100°. Two molecules of iodine were added to an aqueous solution of potassic dehydro-

[1] Proc. Am. Acad., **21**, 145; Ann. Chem. (Liebig), **232**, 55.

mucate, together with potassic iodide in sufficient quantity to carry the iodine into solution. After heating for two hours at 120°, the solution was found to be decolorized and an insoluble product had separated. This product was then collected in ether, and the pale yellow residue left by the ether recrystallized from dilute alcohol. The body thus obtained crystallized in colorless plates, which melted at 47° and gave the percentage of iodine required by a diiodfurfuran.

0.1002 gram substance gave 0.1471 gram AgI.

	Calculated for $C_4H_2I_2O$.	Found.
I	79.34	79.32

This *aa'*-diiodfurfuran is readily soluble in all ordinary organic solvents, but may be crystallized from dilute alcohol. With bromine it yields at once dibromfurfuran tetrabromide with the separation of iodine.

We were further interested to investigate the action of bromine upon an alkaline solution of monoethyl dehydromucate. Although we did not succeed in finding the conditions necessary to give a smooth reaction our results leave no doubt that δ-brompyromucic acid is thus formed. If a solution of monoethyl dehydromucate is made alkaline with potassic carbonate and 1 molecule of bromine is then added, the liquid soon grows turbid with the separation of a colorless oil. This oil, when extracted with ether, was found to possess the characteristic odor of ethyl δ-brompyromucate and solidified at low temperature. On the addition of alcoholic potassic hydrate a crystalline potassium salt was formed. The acid liberated with hydrochloric acid was sparingly soluble in cold water, and crystallized from hot water in shining leafy plates, which melted at 182°. According to Hill and Sanger[1] brompyromucic acid melts at 183° to 184° and its ethyl ester at 17°.

We also attempted to prepare in the same way the corresponding iodine derivative of pyromucic acid, but without success.

aa'-Dibenzoyl Furfuran, $C_{18}H_{12}O_3$.—This ketone may easily be made by acting upon a solution of dehydromucyl chloride in benzol with aluminic chloride. Several different methods

[1] *Loc. cit.*

of preparation were tried, and the best results were obtained in the following manner: 27 grams of the acid chloride were dissolved in 40 grams of benzol and the solution allowed to drop slowly into a boiling solution of 50 grams of aluminic chloride in an equal weight of benzol. After the reaction was over the product was isolated in the usual way and recrystallized from ligroin or alcohol. The weight of the ketone obtained was at least equal to that of the acid chloride taken, and in the case given above the yield was 37 grams, or 96 per cent of the theoretical amount.

I. 0.2026 gram substance gave 0.5843 gram CO_2 and 0.0881 gram H_2O.

II. 0.2038 gram substance gave 0.5871 gram CO_2 and 0.0880 gram H_2O.

	Calculated for $C_{18}H_{12}O_3$.	Found. I.	II.
C	78.26	78.65	78.57
H	4.38	4.86	4.83

The $\alpha\alpha'$-dibenzoyl furfuran crystallizes from alcohol or ligroin in lustrous needles, which melt at 107° (corr.) and sublime at higher temperature. It is readily soluble in cold benzol, chloroform, or glacial acetic acid, sparingly soluble in cold ligroin or carbonic disulphide, somewhat less sparingly soluble in cold alcohol; it is also sparingly soluble in ether.

By the action of various reducing agents upon the ketone we were unable to obtain any well-defined products. Even with red phosphorus and hydriodic acid an amorphous, sticky body was obtained which did not invite further study. With dry bromine, substitution slowly takes place, and a bromine derivative of high melting-point is formed which we have not further examined. Aqueous bromine has little effect under ordinary pressures, but at 140°, in a sealed tube, reaction sets in and dibrommaleic and brombenzoic acids are formed. The acids were extracted with sodic carbonate, the solution filtered from the unaltered ketone, and acidified. The acid which separated melted at 140° to 141° and contained the percentage of bromine required by a brombenzoic acid.

0.1530 gram substance gave 0.1436 gram AgBr.

	Calculated for $C_7H_5BrO_3$.	Found.
Br	39.78	39.94

A closer examination of this acid showed that it contained all three isomers. From the sparingly soluble barium salt was obtained an acid which melted at 153° (uncorr.) after one recrystallization from water, and which was therefore *m*-brombenzoic acid. The readily soluble barium salt yielded a sparingly soluble acid which melted at 245° (uncorr.), and a more readily soluble acid which melted at 142° to 143° (uncorr.); these were evidently the para and ortho acids which melt at 251° and 147°, respectively. The acid liquid from which the brombenzoic acids had separated was extracted with ether and the ether evaporated. The crude acid thus obtained was neutralized with baric hydrate, and the barium salt precipitated from aqueous solution by the addition of a small amount of alcohol. The salt, when recrystallized from water, had the characteristic form of baric dibrommaleate, and the acid prepared from it could be converted by sublimation into the flattened needles of the dibrommaleic anhydride melting at 113°.

On boiling the ketone with diluted nitric acid (sp. gr. 1.30) no action was observed, and the oxidation was not well marked until the specific gravity of the nitric acid reached 1.40. After boiling with an acid of this strength for five hours, the excess of the nitric acid was driven off and the residue extracted with sodic carbonate. A large part of the product proved to be insoluble in the alkaline solution, but this neutral body dissolved readily in alcohol, leaving a very small quantity of a white crystalline substance, which melted at 194° to 195° (uncorr.). The alcoholic solution, when mixed with glacial acetic acid, deposited a crystalline body which was readily soluble in cold benzol or chloroform, insoluble in carbonic disulphide, but which could be recrystallized from alcohol. The body then melted at 130° to 131° (uncorr.), and contained a percentage of nitrogen which showed that it was a mononitro derivative of the ketone; it was not further studied.

0.2002 gram substance gave 8.5 cc. moist nitrogen at 27° and under a pressure of 756 mm.

	Calculated for $C_{18}H_{11}NO_5$.	Found.
N	4.37	4.64

The acids formed by the action of the nitric acid upon the ketone were precipitated from the alkaline solution on the addition of hydrochloric acid. An analysis of the silver salt gave a percentage of silver which agreed with that required by an argentic nitrobenzoate.

0.1095 gram salt gave 0.0747 gram AgBr.

	Calculated for $AgC_7H_4NO_4$.	Found.
Ag	39.39	39.18

Fractional crystallization of the barium salt showed that it was a mixture of the three possible isomers. The readily soluble part of the salt yielded an acid melting at 143° to 144° (uncorr.), which was evidently the *o*-nitrobenzoic acid; the most sparingly soluble salt gave the meta acid melting at 139° (uncorr.), while from the intermediate portion an acid was obtained which melted at 220° to 225° (uncorr.), and which was therefore essentially the *p*-nitrobenzoic acid.

αα'-Dibenzoyl Furfuran Diphenylhydrazone, $C_{30}H_{24}N_4O$.—The ketone was dissolved in fourteen times its weight of glacial acetic acid, an excess of phenylhydrazine added, and the solution heated for some time on the water-bath. On cooling, the dihydrazone separated in bright-yellow, finely felted needles which were recrystallized from hot glacial acetic acid.

0.2207 gram substance gave 25.6 cc. moist nitrogen at 25° and under a pressure of 758 mm.

	Calculated for $C_{30}H_{24}N_4O$.	Found.
N	12.31	12.84

The dihydrazone is readily soluble in chloroform or benzene, but sparingly soluble in alcohol, ether, or glacial acetic acid. When quickly heated it melts promptly at 155° to 156° (corr.), but when slowly heated it melts at a much lower temperature.

αα'-Dibenzoyl Furfuran Dioxime, $C_{18}H_{14}N_2O_3$.—Hydroxylamine reacts readily upon the ketone in alcoholic solution when an excess of sodic hydrate is added as recommended by Auwers.[1] We have added to the ketone, suspended in fifteen

[1] Ber. d. chem. Ges., **22**, 604.

times its weight of alcohol, 3 molecules of hydroxylamine hydrochlorate and 6 molecules of sodic hydrate, each dissolved in a little water. The reaction soon begins and is apparently completed on long standing at ordinary temperatures, but we have usually heated the mixture for several hours on the water-bath. After the evaporation of the alcohol, with the addition of water, the oxime was precipitated with carbonic dioxide. The weight of the product obtained was somewhat greater than that of the ketone taken and amounted to 93.5 per cent of the calculated weight of dioxime. The behavior of the substance in a capillary tubes led us to think that it was not homogeneous, and on crystallization from alcohol it proved to contain at least two different bodies, one of which crystallized in long, slender needles, the other in small, granular aggregations. The solubility of these two bodies in alcohol did not differ sufficiently to enable us to separate them sharply, but no other solvent was found which would answer the purpose better. The most satisfactory method of separation which we have discovered depends upon the different solubilities of the sodium salts of the two bodies in dilute solutions of sodic hydrate, and the readiness with which one of these salts is hydrolyzed in dilute aqueous solution. The hydrolytic dissociation of the sodium salts of oximes was suggested by V. Meyer[1] for the separation of isomeric forms. While the method we describe leaves much to be desired, it has enabled us to separate two bodies which differ widely in properties, and the intermediate fractions have given every indication that they are made up of mixtures of these two substances alone.

The mixed oximes are suspended in a little water and rather more than 2 molecules of sodic hydrate added in concentrated solution. To the gently warmed, clear solution is then added rather less than 4 molecules of sodic hydrate, the concentration being so adjusted that each cubic centimeter of the final solution contains about 150 milligrams of the mixed oximes and 120 milligrams of sodic hydrate. On standing, a crystalline sodium salt separates which is collected after the lapse of twenty-four hours, washed with a little double normal sodic

[1] Ann. Chem. (Liebig), **264**, 116.

hydrate and drained as completely as possible on the pump. The salt thus obtained dissolves readily in a small amount of warm water, but if the solution is diluted hydrolytic dissociation takes place, slowly at ordinary temperatures; rapidly on heating with the separation of the clustered needles of the α-dioxime. The alkaline solution from which the α-dioxime has thus separated contains both forms of the dioxime, which are then precipitated together by carbonic dioxide and again dissolved in sodic hydrate of the proper concentration. The original alkaline mother-liquor, from which the α-sodium salt has crystallized, contains chiefly the β-dioxime, but we have found no method for its purification beyond the removal of the α-dioxime as completely as possible by the use of a still more concentrated solution of sodic hydrate and the repeated recrystallization from alcohol of the oxime thrown down by carbonic dioxide from this strongly alkaline solution.

Both forms of the dioxime are readily soluble in acetone or ethyl acetate, and are precipitated from these solutions on the addition of ligroin. They are both sparingly soluble in alcohol, although the α-dioxime dissolves the more freely, and still more sparingly soluble in ether, chloroform, or benzol. We have not succeeded in preparing any derivatives which could be utilized in their separation or identification. We have also as yet been unable to obtain definite products from Beckmann's molecular rearrangement; the α-dioxime here is apparently converted into the more stable β-modification, and the same conversion may be brought about by heat.

The analysis of the α-dioxime gave the following results:

I. 0.2365 gram substance gave 0.6118 gram CO_2 and 0.1046 gram H_2O.

II. 0.2014 gram substance gave 16.4 cc. moist nitrogen at 15° and under a pressure of 749 mm.

	Calculated for $C_{18}H_{14}N_2O_3$.	Found. I.	Found. II.
C	70.57	70.57	....
H	4.61	4.95	....
N	9.18	....	9.35

The α-dioxime crystallizes from hot alcohol in long, slender needles, which melt at 213°–214° (uncorr.) when quickly

heated. The melted substance occasionally solidifies again at higher temperature, or if solidified by cooling it melts at a higher point. The pure substance was therefore quickly melted and immediately cooled. The hot alcoholic solution then deposited with the needles of the α-dioxime the granular aggregations of the β-modification. A partial separation through the sodium salts showed that the latter amounted to at least 40 per cent of the α-dioxime taken, and the body, after one crystallization from alcohol, melted at 241° to 243° (uncorr.).

The β-dioxime, separated as completely as possible from the α-modification by the process just described, was precipitated with carbonic dioxide, extracted with small quantities of boiling alcohol, and finally recrystallized from a larger amount of the same solvent. It is deposited in minute, irregular plates which are usually grouped in granular clusters. When quickly heated it melted at 243° to 245° (uncorr.); but at this temperature decomposition sets in almost immediately, and the melting-point was much lower if the substance was slowly heated.

I. 0.2316 gram substance gave 0.5972 gram CO_2 and 0.1018 gram H_2O.

II. 0.2062 gram substance gave 17.2 cc. N over KOH (1 : 2) at 18°.5 and under a pressure of 750 mm.

	Calculated for $C_{12}H_{14}N_2O_6$.	Found. I.	II.
C	70.57	70.35	....
H	4.61	4.92	....
N	9.18	....	9.51

CXXII.—On the Reduction of Dehydromucic Acid.[1]

By Henry B. Hill and Alvin S. Wheeler.

In repeating the work of Seelig upon the reduction of dehydromucic acid we were able to profit by the results obtained in recent years by v. Baeyer and his pupils in the study of the reduction of the analogous aromatic dibasic acids. In the light of their experience there seemed to be little doubt that Seelig's

[1] The work described in the following paper formed a part of a thesis presented to the Faculty of Arts and Sciences of Harvard University, in May, 1900, by Alvin S. Wheeler, candidate for the degree of doctor of philosophy.

acid melting at 146° was the direct product of the reduction, and that the isomeric acid melting at 173° was formed from it by the action of the sodic hydrate set free in the reaction. That Schrötter was unable to isolate the second form of the acid was then due in part to his method of reduction, and in part to an insufficient examination of his product. Seelig used a large excess of sodium amalgam, at ordinary temperature, without neutralizing the sodic hydrate which was formed. We reduced the sodium to one-fifth the amount used by him, carried on the reaction at 0°, in a much more concentrated solution, and at the same time passed a rapid stream of carbonic dioxide into the solution. Under these conditions but little of the higher melting isomer was formed. The latter acid becomes the main product, if the reduction is carried on at ordinary temperature without neutralizing the sodic hydrate, and the alkaline solution is then heated to boiling. Reduction is readily effected when the dehydromucic acid is suspended in ten times its weight of water, neutralized with sodic carbonate, and thirty-five times its weight of finely divided 3 per cent sodium amalgam added. The time required to complete the reaction depends upon the subdivision of the amalgam, but is usually about two hours. Since the products of the reduction are readily soluble in water the reaction is very nearly completed as soon as hydrochloric acid fails to precipitate any unaltered dehydromucic acid. We have also reduced dehydromucic acid by the electrolysis of a solution of its sodium salt containing 10 per cent of the acid. This mode of reduction, however, did not appear to us to offer any advantage over the use of sodium amalgam.

The isolation of the acids which are formed was at first a matter of some difficulty. Although they may be extracted from aqueous solution by ether, the process is slow and involves a great deal of labor by the ordinary method with separatory funnel. Evaporation to dryness and extraction of the pulverized residue in a Soxhlet extractor was more advantageous, but still far from convenient. The method finally adopted was the use of a slightly modified form of automatic extractor for liquids described by Göckel.[1] The side tube

[1] Zeit. angew. Chem., 1897, 683; Chem. Centrbl., 1897, II., 1169.

recommended by Göckel seemed to us a needless complication, and we found a plain straight jacket-tube to answer the purpose admirably. The alkaline solution, poured off from the mercury, was made feebly acid to litmus, concentrated to a convenient volume, strongly acidified with hydrochloric acid, and completely extracted with ether. So efficient was the automatic extractor that 89 per cent of the lower-melting (α)-acid contained in the solution could be extracted in five hours. A partial separation of the two isomeric acids can be effected in the course of the extraction, since the α-acid is more readily taken up, and the product obtained toward the end of the extraction is mainly β-acid. The crude acid left by the evaporation of the ether formed a light-colored, crystalline mass, while Seelig obtained a syrup which slowly crystallized when allowed to stand in a desiccator. It seems to us probable that his product contained, in addition to the two acids which he described, the γ-acid which we mention later, and possibly also the tetrahydrofurfuran-$\alpha\alpha'$-dicarboxylic acid formed from this acid by reduction. The weight of the product which we obtained was very nearly that required by theory.

In the separation of the two isomeric acids which form the main part of the product we used at first the barium salts as recommended by Seelig; a more careful study showed us that the lead salts were far better adapted to the purpose. If the mixed acids are dissolved in thirty times their weight of water and the solution boiled with baric carbonate, a solution is obtained which deposits, on cooling, the pulverulent salt of the α-acid. On spontaneous evaporation six-sided plates separate, which are also a salt of the α-acid, but with 4.5 molecules of water, while the pulverulent salt contains two. When the solution is then concentrated to small volume it becomes pasty with the separation of the salt of the β-acid, necessarily with some admixture of the α-salt. The mother-liquor, by spontaneous evaporation, then leaves a varnish which resembles that given under like conditions by a solution of the barium salt of the γ-acid. While the sparingly soluble salt of the α-acid could easily be purified by recrystallization, the more soluble salt of the β-acid could not readily

be isolated in a pure condition. Although the difference in the solubility of the lead salts of the two acids at ordinary temperatures proved to be less than that of the barium salts, the solubility of the salt of the α-acid was largely increased by heat, while that of the salt of the β-acid was little more than doubled. The crude acid was therefore dissolved in about one hundred times its weight of water, boiled with an excess of plumbic carbonate and the hot solution stirred to promote the separation of the salt of the β-acid. The solution quickly filtered then deposited almost the whole of the salt of the α-acid in the form of bulky needles, which may be purified by recrystallization from boiling water. On treating the β-salt with small quantities of boiling water all admixture of the more soluble α-salt is removed. Although we have found it easy to prepare a crude acid which should contain chiefly one isomer or the other, a careful examination has invariably shown both acids present. While the γ-acid was also probably present, especially when the β-acid was the chief product, the quantity was so small that it gave no trouble. In the preparation of the γ-modification we have taken pains to carry the reaction so far that all the β-acid was isomerized.

α-Dihydrofurfuran-$\alpha\alpha'$-dicarboxylic Acid.

The preparation of the lead salt of this acid has just been described. We have usually suspended the salt in water, set free the acid with hydrogen sulphide, evaporated the aqueous solution to dryness, and recrystallized the residue from ether. If the reduction is carried on at 0° and a rapid stream of carbonic dioxide is passed into the solution, almost the whole product consists of this acid. It dissolves in about twice its weight of cold water and is still more readily soluble in hot water; from aqueous solution it crystallizes in friable, leafy plates, which are anhydrous. It dissolves readily in alcohol or in ether and frequently crystallizes from the latter solvent in large, rectangular plates; it is very sparingly soluble in chloroform and insoluble in benzol or ligroin; from a mixture of ether and ligroin it crystallizes in the form of needles. The pure acid melts at 149° to 150° (corr.).

An analysis gave the following results:

0.2108 gram substance gave 0.3526 gram CO_2 and 0.0715 gram H_2O.

	Calculated for $C_6H_6O_6$.	Found.
C	45.55	45.62
H	3.83	3.79

The barium, calcium, and silver salts of the acid were analyzed by Seelig; we have repeated his work and also studied the lead salt.

Baric α-Dihydrofurfuran-αα'-dicarboxylate, $BaC_6H_4O_5.2H_2O$. The acid was dissolved in thirty times its weight of water and the solution boiled with an excess of baric carbonate. As the filtered solution cools, the greater part of the salt separates in a finely divided condition. The air-dried salt proved to contain 2 molecules of water.

I. 0.3252 gram air-dried salt gave 0.2294 gram $BaSO_4$.

II. 1.1542 grams air-dried salt lost, at 180°, 0.1318 gram H_2O.

	Calculated for $BaC_6H_4O_5.2H_2O$.	Found. I.	Found. II.
Ba	41.71	41.52	....
H_2O	10.93	....	11.42

If a cold solution of this salt is allowed to evaporate spontaneously, large, six-sided plates are deposited which contain 4.5 molecules of water.

1.0122 grams air-dried salt lost, at 190°, 0.2164 gram H_2O.

	Calculated for $BaC_6H_4O_5.4\frac{1}{2}H_2O$.	Found.
H_2O	21.65	21.38

Both of these salts were obtained and analyzed by Seelig.

A cold saturated solution obtained by cooling a hot solution of the barium salt gave the following results:

I. 42.07 grams solution, saturated at 18°, gave 0.0700 gram $BaSO_4$.

II. 48.97 grams solution, saturated at 18°, gave 0.0799 gram $BaSO_4$.

The aqueous solution saturated at 18° therefore contained the following percentages of the anhydrous salt:

I.	II.
0.21	0.20

Calcic α-Dihydrofurfuran-αα'-dicarboxylate, $CaC_6H_4O_5.1\frac{1}{2}H_2O$. —This salt was very readily soluble in water and it was necessary to evaporate the solution to small volume in order to ensure its separation. As the salt proved to be deliquescent, a fact not mentioned by Seelig, it was dried by pressure between folds of filter-paper and analyzed at once. Our analysis showed that it contained but 1.5 molecules of water, while Seelig had found 2.5.

1.0897 grams salt lost, at 180°, 0.1270 gram H_2O.

	Calculated for.	Found.
H_2O	12.12	11.65

0.2062 gram salt, dried at 180°, gave 0.1436 gram $CaSO_4$.

	Calculated for.	Found.
Ca	20.40	20.46

Argentic α-Dihydrofurfuran-αα'-dicarboxylate, $Ag_2C_6H_4O_5.\frac{1}{2}H_2O$.— Our analyses of the air-dried silver salt confirmed the conclusion of Seelig that it contained 0.5 molecule of water which could not be expelled by heat without decomposition. At 125° it lost but 0.38 per cent of its weight, while the calculated loss for 0.5 molecule of water is 2.36 per cent; even at this temperature decomposition soon set in.

0.2169 gram air-dried salt gave 0.1632 gram AgCl.

	Calculated for $AgC_6H_4O_5.\frac{1}{2}H_2O$.	Found.
Ag	56.66	56.62

Plumbic α-Dihydrofurfuran-αα'-dicarboxylate, $PbC_6H_4O_5.2H_2O$. —This salt was made by neutralizing with plumbic carbonate a boiling solution of the acid in one hundred times its weight of water. As the filtered solution cools the salt separates in bulky, opaque needles which, on long standing, are converted into compact, transparent plates. Occasionally these plates were formed at first on slow cooling of the solution. Analyses showed that the two forms of the salt had the same composition.

I. 1.4919 grams air-dried needles lost, at 180°, 0.1371 gram H_2O.

II. 1.1808 grams air-dried plates lost, at 165°, 0.1090 gram H_2O.

	Calculated for $PbC_6H_4O_5.2H_2O$.	Found. I.	II.
H_2O	9.01	9.19	9.23

0.2988 gram anhydrous salt gave 0.2494 gram $PbSO_4$.

	Calculated for $PbC_6H_4O_5$.	Found.
Pb	57.01	57.01

The solubility of the salt in hot water was determined according to the method described by Pawlewski,[1] in addition to its solubility at ordinary temperature. In each case the lead was precipitated as sulphide and weighed as sulphate.

I. 49.69 grams solution, saturated at 20°, gave 0.0191 gram $PbSO_4$.

II. 48.52 grams solution, saturated at 20°, gave 0.0187 gram $PbSO_4$.

The aqueous solution saturated at 20° therefore contained the following percentages of the anhydrous salt.

I.	II.
0.046	0.046

I. 7.470 grams solution, saturated at 99°.5, gave 0.0634 gram $PbSO_4$.

II. 10.077 grams solution, saturated at 99°.5, gave 0.0870 gram $PbSO_4$.

The aqueous solution saturated at 99°.5 therefore contained the following percentages of the anhydrous salt:

I.	II.
1.02	1.03

When the *α-Dihydrofurfuran-αα'-dicarboxylic* acid was heated above its melting-point a slight sublimate was noticed, and at the same time carbonic dioxide was apparently given off. Since it seemed probable that the hydride of pyromucic acid might be formed under these conditions a larger portion of the acid was heated to 190° in a stream of hydrogen. Carbonic oxide was formed in abundance and a large crystalline sublimate was obtained. The more volatile portion had condensed in slender needles, but the greater portion was in massive

[1] Ber. d. chem. Ges., 32, 1040.

form. The slender needles melted at 128° and after resublimation at 130°. They were formed in such small quantity that a more positive identification of them as pyromucic acid was not possible. The whole crystalline product was therefore dissolved in water and the acid solution neutralized with baric carbonate. The barium salt proved to be very sparingly soluble in water, and no appreciable amount of the readily soluble baric pyromucate could be isolated. The insoluble barium salt, when acidified and extracted with ether, gave the unaltered α-acid melting at 146° (uncorr.) in abundance. A large part of the acid had therefore volatilized without decomposition or isomerization.

On heating the acid in a sealed tube with concentrated hydrochloric or hydrobromic acid we found that carbonization ensued at high temperatures and that at lower temperatures the acid remained unchanged. In alkaline solution the acid is unstable and passes first into the β- and finally into the γ-modification. The details of this isomerization will be more fully discussed in describing the preparation of the latter acids. The prolonged action of sodium amalgam had little effect upon the acid, and the greater part of it could be recovered unchanged.

Oxidation with Nitric Acid and Potassium Permanganate.

The α-acid is readily attacked by oxidizing agents, but we have been able to isolate as products of the oxidation only dehydromucic and oxalic acids. When heated with three times its weight of concentrated nitric acid (sp. gr. 1.42) to 60° a quiet reaction took place which was completed in the course of twelve hours. An insoluble substance had separated which amounted to 13 per cent of the weight of the acid taken. This body sublimed without melting and gave, with ferric chloride, the red jelly characteristic for dehydromucic acid. From the solution could be isolated only oxalic acid, which was identified through its calcium salt and its behavior in a capillary tube. The same products were obtained on treating an alkaline solution of the acid with a sufficient quantity of a 4 per cent solution of potassic permanganate to give 4 atoms of oxygen to each molecule of the acid. The oxida-

tion was allowed to proceed at ordinary temperature, and on acidification of the concentrated alkaline solution dehydromucic acid amounting to 20 per cent of the weight of the α-acid taken was obtained. A careful examination of the solution failed to show the presence of any other product of the reaction except oxalic acid.

Action of Bromine.

When equal molecules of the pure α-acid and bromine were heated in a sealed tube to 140° hydrobromic acid was evolved in abundance and dehydromucic acid was almost the only product. If, however, the acid was exposed to an atmosphere of bromine, it gradually gained in weight, and finally it added rather more than its own weight of bromine. The red transparent mass which was thus obtained was allowed to stand for some time over lime, and then crystallized from chloroform. After repeated recrystallization it melted at 141° (uncorr.) and proved to contain (Analysis V) a percentage of bromine which showed that it was formed by the addition of 1 molecule of bromine to the acid. After recrystallization from water and drying over sulphuric acid the melting-point was raised to 145° (uncorr.). With aqueous bromine a slight oxidation takes place, but the main product is the dibromide of the acid, and it may be prepared most conveniently in this way. The acid is dissolved in twice its weight of water and bromine vapor is slowly passed in by a current of air. When 1 molecule of bromine has thus been added crystals of the dibromide separate in abundance, if the solution is vigorously shaken. The product thus obtained amounts to 50 per cent of the theoretical weight, and from the mother-liquor an additional 10 per cent may be obtained. There remains at last a viscous liquid from which no definite products could be isolated. The nature of this viscous product we have been unable to determine; it is also obtained when the bromine is diluted with anhydrous solvents, or when the vapor of bromine is allowed to act upon the dry acid. From the aqueous solution small amounts of carbonic dioxide were evolved, and occasionally we have also noticed the formation of a small amount of dehydromucic acid. It is worthy of note that this

same addition-product was also formed when 2 molecules of bromine were added to an aqueous solution of the potassium salt of the acid.

The product recrystallized from water contained 1 molecule of water, as is shown by the following analyses:

I. 0.2694 gram substance gave 0.2146 gram CO_2; and 0.0585 gram H_2O.

II. 0.1910 gram substance gave 0.2142 gram AgBr.

III. 1.1748 grams substance lost, over sulphuric acid, 0.0641 gram H_2O.

	Calculated for $C_6H_4Br_2O_5.H_2O$.	Found. I.	II.	III.
C	21.43	21.72	....	....
H	2.40	2.42	....	....
Br	47.61	....	47.73	....
H_2O	5.36	....	....	5.46

IV. 0.2090 gram anhydrous substance gave 0.2462 gram AgBr.

V. 0.1586 gram anhydrous substance gave 0.1858 gram AgBr.

	Calculated for $C_6H_6Br_2O_5$.	Found. IV.	V.
Br	50.29	50.14	49.85

The α-dihydrofurfuran-$\alpha\alpha'$-dicarboxylic dibromide is readily soluble in water without essential decomposition and crystallizes in brilliant, four-sided prisms with sharply beveled ends, which melt at 112° to 113° (uncorr.). It is readily soluble in alcohol or in ether, more sparingly soluble in boiling chloroform, from which it crystallizes in rectangular plates. It dissolves very sparingly in hot benzol, and is insoluble in ligroin or carbonic disulphide. The melting-point of the anhydrous body is 147° to 148° (corr.). On treating the aqueous solution with sodium amalgam, or on warming the alcoholic solution with zinc dust the α-acid is reformed. On boiling with water a slow decomposition sets in, accompanied by the escape of carbonic dioxide; in alkaline solution the reaction runs more rapidly.

Action of Baric Hydrate upon α-Dibromide.

The dibromide was dissolved in a little water and 2.5 mole-

cules of baric hydrate were then added. Baric carbonate soon began to separate in the cold, and after standing for twenty-four hours at ordinary temperature the solution was but feebly alkaline. After the removal of the baric carbonate the slight excess of baric hydrate was neutralized with carbonic dioxide and the filtered solution evaporated to a small volume. On cooling, a crystalline salt separated, which was redissolved in a little water and acidified with hydrochloric acid. The highly crystalline acid thus obtained was readily soluble in hot water, contained no trace of bromine, melted at 129° (uncorr.), gave a red-brown precipitate with ferric chloride, and sublimed readily at 100° with the odor of pyromucic acid. The mother-liquor from the baric pyromucate contained baric bromide in abundance. The α-dibromide had therefore been decomposed according to the equation:

$$2C_6H_6Br_2O_5 + 5BaO_2H_2 = (C_5H_3O_3)_2Ba + 2BaCO_3 + 2BaBr_2 + 8H_2O.$$

Careful determination showed that the weight of baric carbonate formed was 92.7 per cent and of the pyromucic acid 92.4 per cent of the amounts demanded by this equation.

Action of Chlorine.

All our attempts to form an addition-product analogous to the bromine derivative just described by the action of dry chlorine upon the α-acid have been unsuccessful. In aqueous solution a crystalline body was easily obtained, but water entered into the reaction, and the product proved to contain hydroxyl as well as chlorine. The pure α-acid was dissolved in twice its weight of water and saturated in the cold with chlorine. On extracting the solution with ether a syrup was obtained which solidified when vigorously stirred. The product may then be purified by recrystallization from a small amount of water. The air-dried substance lost nothing in a desiccator and but a fraction of a milligram when heated for three hours at 125°; at a higher temperature decomposition ensues.

I. 0.2248 gram air-dried substance gave 0.2810 gram CO_2; and 0.0682 gram H_2O.

II. 0.1810 gram air-dried substance gave 0.1242 gram AgCl.

	Calculated for $C_6H_7ClO_6$.	Found. I.	Found. II.
C	34.21	34.10	....
H	3.35	3.39	....
Cl	16.85	....	16.96

This α-chlorhydroxytetrafurfuran-$\alpha\alpha'$-dicarboxylic acid is readily soluble in water and crystallizes in large four-sided prisms with beveled ends. It is readily soluble in alcohol or acetone, more sparingly soluble in ether, and insoluble in ligroin, benzol, chloroform, or carbonic disulphide; it crystallizes well from a mixture of ether and ligroin. The body decomposes at 209° to 210° (corr.). Bromine in aqueous solution seems to have no action upon it, and it is not oxidized by concentrated nitric acid. Acetic anhydride reacts upon it readily and yields a well-crystallized product, which has not yet been further studied.

β-Dihydrofurfuran-$\alpha\alpha'$-dicarboxylic Acid.

The ready isomerization of the α-acid in alkaline solution to the β-modification has already been mentioned, as well as the fact that we have been unable to prepare the α-acid in such a way as to avoid completely this isomerization. The rapidity of the change varies with the temperature and concentration, as also with the nature of the alkaline solution. The preparation of larger quantities of the β-acid is further complicated by its simultaneous partial conversion into the γ-modification. Preliminary experiments showed that the isomerization was but slowly effected by baric hydrate, so that the sparingly soluble barium salt of the α-acid could not conveniently be converted directly into the readily soluble salt of the β-acid; sodic hydrate worked quickly and on the whole was most advantageous. For the isomerization of pure α-acid it was found best to dissolve the acid with an equal weight of sodic hydrate in 20 parts of water, and to boil this solution for an hour with return condenser. Under these conditions about 10 per cent of the α-acid remained unchanged, but not much γ-acid was formed.

The β-acid may be made most conveniently directly from dehydromucic acid by modifying slightly the method of reduction. The dehydromucic acid is suspended in ten times

its weight of water and carried into solution by the addition of sodic carbonate ; 30 parts of a 3 per cent sodium amalgam are then added, and the reduction allowed to proceed at ordinary temperature without neutralizing the sodic hydrate formed in the reaction. When all action is over the decanted solution is boiled for a few minutes, acidified, and extracted with ether. The β-acid is then isolated and purified through its sparingly soluble lead salt, as has already been described in explaining the separation and purification of the α-acid. By this process we have obtained directly from dehydromucic acid, 76 per cent of the theoretical yield of pure β-acid. This acid was obtained in a pure condition by Seelig, and we have been able to confirm essentially all his observations. It dissolves in about four times its weight of cold water, much more readily in hot water, and crystallizes from aqueous solution in large, brilliant, complex forms, which contain 1 molecule of water.

I. 0.2091 gram air-dried substance gave 0.3127 gram CO_2; and 0.0878 gram H_2O.

II. 0.5682 gram air-dried substance lost, at 110°, 0.0574 gram H_2O.

	Calculated for $C_6H_6O_5.H_2O$.	Found. I.	II.
C	40.91	40.81	....
H	4.58	4.69	....
H_2O	10.23	....	10.10

The β-dihydrofurfuran-$\alpha\alpha'$-dicarboxylic acid is readily soluble in alcohol, but more sparingly soluble in ether; it is so much less readily soluble in ether than the α-acid that a partial separation of the two acids is effected in extracting with ether the aqueous solution. It is insoluble in chloroform, benzol, or ligroin, but may be obtained in stout needles from solution in a mixture of ether and ligroin. The anhydrous acid melts at 178° to 179° (corr.) ; the hydrous acid collapses with the loss of water above 100°.

In addition to the barium, calcium, and silver salts, which were investigated by Seelig, we have studied also the lead salt.

Baric α-Dihydrofurfuran-αα'-dicarboxylate, $BaC_6H_4O_5.1\frac{1}{2}H_2O$. —A hot concentrated solution of the acid was neutralized with baric hydrate, the mother-liquor drained from the salt which separated on cooling, and the solid well washed with cold water. The air-dried salt then had the composition assigned to it by Seelig.

0.6853 gram air-dried salt lost, at 185°, 0.0600 gram H_2O.

	Calculated for $BaC_6H_4O_5.1\frac{1}{2}H_2O$.	Found.
H_2O	8.43	8.76

0.1996 gram anhydrous salt gave 0.1574 gram $BaSO_4$.

	Calculated for $BaC_6H_4O_5$.	Found.
Ba	46.82	46.40

The solubility of the salt in cold water was also determined.

6.877 grams of solution saturated at 20° gave 0.0766 gram $BaSO_4$.

Hence the aqueous solution saturated at 20° contained 1.40 per cent of the anhydrous salt.

Calcic β-dihydrofurfuran-αα'-dicarboxylate, $CaC_6H_4O_5.2\frac{1}{2}H_2O$. —This salt, prepared by neutralizing an aqueous solution of the acid with calcic carbonate, was very readily soluble in water, and a hot concentrated solution gelatinized on cooling. The gelatinous mass, on exposure to the air, gave a permanent, solid salt which apparently contained 2.5 molecules of water. Seelig prepared a salt by precipitating the aqueous solution with alcohol, which contained 1.5 molecules.

I. 0.2229 gram air-dried salt gave 0.1251 gram $CaSO_4$.

II. 0.9922 gram air-dried salt lost, at 200°, 0.1794 gram H_2O.

	Calculated for $CaC_6H_4O_5.2\frac{1}{2}H_2O$.	Found. I.	Found. II.
Ca	16.59	16.50	....
H_2O	18.68	....	18.08

0.2150 gram anhydrous salt gave 0.1468 gram $CaSO_4$.

	Calculated for. $CaC_6H_4O_5$.	Found.
Ca	20.40	20.07

Argentic β-Dihydrofurfuran-αα'-dicarboxylate, $Ag_2C_6H_4O_5$.—The silver salt crystallizes in microscopic needles which are not very sparingly soluble in cold water, but the solubility is not much increased by heat.

0.2025 gram air-dried salt gave 0.1562 gram AgCl.

	Calculated for $Ag_2C_6H_4O_5$.	Found.
Ag	58.03	58.05

Plumbic β-Dihydrofurfuran-αα'-dicarboxylate, $PbC_6H_4O_5.H_2O$.—This salt was prepared for analysis by precipitating with plumbic nitrate a solution of the ammonium salt of the acid. The air-dried salt contained 1 molecule of water, one-half of which is lost at 195°; at higher temperature decomposition sets in. From boiling water it was deposited in small, clear, rhombic plates.

I. 0.1849 gram air-dried salt gave 0.1463 gram $PbSO_4$.

II. 0.2510 gram air-dried salt gave 0.1993 gram $PbSO_4$.

III. 1.0127 grams air-dried salt lost, at 195°, 0.0235 gram H_2O.

IV. 0.9390 gram air-dried salt lost, at 195°, 0.0213 gram H_2O.

	Calculated for $PbC_6H_4O_5.H_2O$.	Found. I.	II.	III.	IV.
Pb	54.31	54.05	54.24	....	....
$\frac{1}{2}H_2O$	2.36	....	....	2.32	2.27

The solubility of the salt in hot and cold water was also determined by the methods used in the case of the lead salt of the α-acid.

I. 87.51 grams solution, saturated at 20°, gave 0.0085 gram $PbSO_4$.

II. 96.76 grams solution, saturated at 20°, gave 0.0109 gram $PbSO_4$.

The solution saturated at 20° therefore contained the following percentages of the anhydrous salt:

I.	II.
0.012	0.013

I. 54.88 grams solution, saturated at 99°.5, gave 0.0152 gram $PbSO_4$.

II. 59.41 grams solution, saturated at 99°.5, gave 0.0111 gram $PbSO_4$.

The solution saturated at 99°.5 therefore contained the following percentages of the anhydrous salt:

I.	II.
0.032	0.022

On heating the β-dihydrofurfuran-αα′-dicarboxylic acid with fuming hydrobromic acid to 100° we found that it remained unchanged, while at 150° carbonization ensued. A 10 per cent solution of the acid was treated with a large excess of sodium amalgam, but nearly the whole amount taken was recovered unchanged. On long boiling with a solution of sodic hydrate the acid was completely isomerized into the γ-modification which is described later.

Oxidation with Nitric Acid and Potassic Permanganate.

Concentrated nitric acid (sp. gr. 1.42) oxidizes the β-acid readily at 100°; we found that the reaction ran quietly, and at the end of three hours was apparently complete. Dehydromucic acid, amounting to about 20 per cent of the weight of the β-acid taken, had then separated and was fully identified by its behavior in a capillary tube and its reaction with ferric chloride. From the mother-liquor nothing but oxalic acid could be isolated. Permanganate in alkaline solution was immediately decolorized, but after the addition of a sufficient quantity to give 4 atoms of oxygen to each molecule of the acid, nothing but oxalic acid could be isolated from the concentrated solution. If dehydromucic acid was formed in the reaction it was only in insignificant quantity.

Action of Bromine.

When exposed to the vapor of bromine at ordinary temperature the acid slowly gained in weight, but after three days this gain amounted to but 28 per cent of that required by the addition of one molecule of bromine, and a part of this was again lost on standing over lime. At 140°, in a sealed tube, an addition-product was formed, but at the same time a certain amount of hydrobromic acid was evolved and small quantities of dehydromucic acid could be detected. Dilution with

chloroform gave no satisfactory results, but the addition-product could easily be formed in aqueous solution. Bromine vapor was passed into a saturated aqueous solution of the acid by means of a current of air; the color of the bromine rapidly disappeared, and when 1 molecule had been taken up a crystalline precipitate separated spontaneously or after shaking the solution. The product may then be crystallized from water and forms four-sided, obliquely truncated prisms which contain 2 molecules of water.

I. 0.1865 gram air-dried substance gave 0.1974 gram AgBr.

II. 0.7475 gram air-dried substance lost, at 105°, 0.0750 gram H_2O.

	Calculated for $C_6H_6Br_2O_6.2H_2O$.	Found. I.	II.
Br	45.17	45.05	....
H_2O	10.18	....	10.03

0.2018 gram anhydrous substance gave 0.2389 gram AgBr.

	Calculated for $C_6H_6Br_2O_5$.	Found.
Br	50.29	50.40

The β-dihydrofurfuran-αα′-dicarboxylic dibromide is readily soluble in alcohol or ether, but slightly soluble in hot benzol or chloroform, and is insoluble in ligroin or carbonic disulphide. In a capillary tube it decomposes at 213° to 214° (corr.). Sodium amalgam reduces it readily to the β-acid. On boiling the aqueous solution a slow decomposition sets in; apparently the same decomposition takes place rapidly in alkaline solution.

Action of Baric Hydrate on β-Dibromide.

To a cold aqueous solution of the β-dibromide was added 2.5 molecules of baric hydrate. After standing for thirty-six hours the feebly alkaline solution was filtered from the baric carbonate which had separated, the slight excess of baric hydrate removed with carbonic dioxide, and the clear solution evaporated to a small volume. The crystalline barium salt which was obtained as the solution cooled gave, on acidification, an abundant separation of pyromucic acid, which melted at 130° (uncorr.), sublimed readily at 100°, and gave a red-

brown precipitate with ferric chloride. Baric bromide had also been formed in abundance. The reaction was therefore identical with that which he had observed in the case of the corresponding α-compound.

$$2C_6H_6Br_2O_5 + 5BaO_2H_2 = (C_5H_3O_3)_2Ba + 2BaCO_3 + 2BaBr_2 + 8H_2O.$$

The weight of the baric carbonate formed was 90 per cent and that of the baric pyromucate 88.5 per cent of the amount required by this equation.

Action of Chlorine.

The β-acid was dissolved in four times its weight of water, the solution cooled with ice, and saturated with chlorine. On extraction with ether a thick syrup was obtained, which solidified on stirring. The body may then be crystallized from a small amount of water or from ether. It forms large, obliquely truncated prisms, which melt at 95° and contain 1.5 molecules of water. The yield amounts to about 33 per cent of the weight of the β-acid taken.

0.9201 gram air-dried substance lost, over sulphuric acid, 0.1041 gram H_2O.

	Calculated for $C_5H_7ClO_6.1\frac{1}{2}H_2O$.	Found.
H_2O	11.38	11.32

0.2031 gram substance, dried over sulphuric acid, gave 0.1408 gram AgCl.

	Calculated for $C_5H_7ClO_6$.	Found.
Cl	16.85	17.14

Like the corresponding derivative of the α-acid this body reacts with acetic anhydride and forms a crystalline product, which has not been further studied.

γ-Dihydrofurfuran-$\alpha\alpha'$-Dicarboxylic Acid.

In studying the formation of the β-acid it soon became evident that the yield of this acid was greatly diminished, if the action of the sodic hydrate was carried too far. At first we assumed that this loss was due to the formation of products of

a radically different nature; but when we discovered that the α- and β-acids were merely stereometrically different forms of the same structure, and that the difference between them was not conditioned by an alteration in the position of the double bond, we determined to push the reaction to its limit. Pure α-acid was accordingly dissolved in ten times its weight of water, and twice its weight of sodic hydrate was added; the solution was then heated upon the water-bath for sixteen hours in a silver flask, the solution acidified and extracted with ether in the apparatus already described. In a short time a crystalline acid, very sparingly soluble in ether, began to separate in the flask, and when the extraction was complete the weight of the new acid obtained was substantially equal to that of the α-acid taken. Analysis showed that this was a third or γ-modification of the dihydrofurfuran-$\alpha\alpha'$-dicarboxylic acid. Its preparation in quantity, directly from dehydromucic acid, was a simple matter. A solution of sodic dehydromucate, containing 10 per cent of the acid, was reduced at ordinary temperature with finely divided 3 per cent sodium amalgam; 30 grams of the amalgam were used for each gram of the acid. After twenty-four hours the strongly alkaline solution was decanted from the mercury, filtered, and boiled for sixteen hours in a silver flask fitted with a return cooler. The solution was then acidified and thoroughly extracted with ether. In this way 84 per cent of the theoretical yield of crude acid may be obtained, and it is so sparingly soluble even in boiling ether that its purification is a matter of no difficulty. For analysis it was further recrystallized several times from water. The air-dried acid lost nothing in weight over sulphuric acid.

0.2114 gram substance gave 0.3528 gram CO_2; and 0.0726 gram H_2O.

	Calculated for $C_6H_8O_5$.	Found.
C	45.55	45.52
H	3.83	3.84

The γ-acid is readily soluble in cold water and crystallizes from warm aqueous solution in stellate clusters of plates. It dissolves readily in alcohol, but requires nearly 200 parts of

boiling ether for its solution; hot glacial acetic acid dissolves it freely, but the greater part is again deposited on cooling; it is insoluble in chloroform, ligroin, or benzol. In a capillary tube the acid decomposes without melting, but the temperature varies greatly with the time; at 170° the time required was found to be eleven minutes, while ten seconds sufficed at 210°. If the substance was introduced into the bath and the temperature raised at the usual rate, decomposition took place at about 194° (uncorr.). As the decomposition was attended by the escape of carbonic dioxide a determination of the amount thus given off was made. It was found, however, that the total loss in weight at 170° was but 9.51 per cent and that a part of this, 2.20 per cent, was due to the formation of water, while a loss of 27.84 per cent was required by the formation of 1 molecule of carbonic dioxide.

The γ-acid was discovered toward the end of our investigation, and we have been unable as yet to make a systematic study of its salts. We have been obliged to content ourselves with the study of its reduction and oxidation, and the product formed from it by the addition of bromine.

Action of Sodium Amalgam.

While the α- and β-acids are not affected by nascent hydrogen the γ-acid is reduced in alkaline solution, although a large excess of sodium amalgam seems to be necessary to complete the reaction. The products formed are two stereoisomeric forms of the tetrahydrofurfuran-$\alpha\alpha$-dicarboxylic acid, which were recently described by Lean.[1] We had just succeeded in isolating these two acids by a method quite different from Lean's when his paper reached us. Our own observations agreed so closely with the description of his results that we thought it unnecessary to carry our investigations further.

The γ-acid was dissolved in twenty times its weight of water and neutralized with sodic carbonate; 125 grams of a 3 per cent sodium amalgam were then added for each gram of the acid, the mixture heated upon a water-bath, and a rapid stream of carbonic dioxide passed into the solution. When

[1] J. Chem. Soc., 77, 103.

the action was over, the liquid was acidified and extracted with ether. The viscous product obtained gradually solidified, but gave no indication of a definite melting-point. It was therefore dissolved in two hundred times its weight of water and the boiling solution neutralized with plumbic carbonate. The filtered solution proved to contain the whole of the lead salts formed, and as concentration failed to cause the separation of any noticeable quantity of salt it was evaporated to dryness. The residue consisted of white, opaque crystals embedded in a transparent varnish. On the addition of a little cold water the whole mass grew opaque and increased considerably in bulk. It was then found that the salt was no longer readily soluble in water, but that little more than 0.5 of it was dissolved by 70 parts of boiling water. The soluble and insoluble portions were therefore separately acidified and extracted with ether. From the insoluble portion an acid was obtained which was indifferent to bromine and which melted completely, though not sharply, at 95°. After recrystallization from water it melted at 59° to 61°, and on dehydration over sulphuric acid the melting-point again rose to 94° to 95°. The acid was readily soluble in water or alcohol, more sparingly soluble in ether, and insoluble in chloroform, ligroin, or benzol. It could easily be recrystallized from concentrated hydrochloric acid as recommended by Lean. These properties sufficiently identify it as one of the tetrahydrofurfuran-$\alpha\alpha'$-dicarboxylic acids described by Lean. The acid obtained from the soluble lead salt melted at 115° to 116°, but this melting-point was easily raised to 124° by recrystallization from a mixture of ether and ligroin. It was readily soluble in water, alcohol, or glacial acetic acid, more sparingly soluble in ether, and insoluble in chloroform, ligroin, or benzol. From boiling toluol it crystallized in leafy aggregations. This acid agrees with the description given by Lean of the second form of his tetrahydrofurfuran-$\alpha\alpha'$-dicarboxylic acid.

Oxidation with Nitric Acid and Potassic Permanganate.

The γ-acid was much more readily attacked by nitric acid than either the α- or the β-acid; even a diluted acid (sp. gr. 1.25) reacted vigorously at 100°. The products formed proved

to be oxalic acid and a small amount of dehydromucic acid. These two acids were also formed by oxidation with permanganate in alkaline solution, although the amount of dehydromucic acid obtained was extremely small.

Action of Bromine.

The γ-acid is readily attacked by bromine, but we have been unable to prepare in a pure condition the addition-product which is formed. Little or no crystalline product could be obtained either by exposure to bromine vapor or by adding bromine to an aqueous solution of the acid. Preliminary experiments showed that chloroform was the only anhydrous diluent that promised to give satisfactory results, and in this case the insolubility both of the acid and its dibromide made its use inconvenient or impracticable. By the addition of a small amount of glacial acetic acid this difficulty was obviated, but the product which we obtained contained too small a percentage of bromine. As the evolution of hydrobromic acid was always noticed the product doubtless contained an admixture of the corresponding substituted acid. The most successful preparations were made as follows: 15 grams of dry chloroform were mixed with 2.5 grams of glacial acetic acid (99.5 per cent) and 1 gram of bromine; 1 gram of pure γ-acid was then added, the mixture shaken thoroughly, and the solution quickly filtered from the small amount of unaltered γ-acid; the separation of prismatic crystals of the dibromide begins at once and the separation is soon complete. The crude product, which amounts to 50 per cent of the theoretical yield, is then purified by washing with boiling benzol, to which a few drops of pure acetone have been added. The substance may also be recrystallized from a mixture of ether and ligroin, and the material used in Analysis III was thus prepared.

I. 0.1802 gram substance gave 0.2058 gram AgBr.
II. 0.2009 gram substance gave 0.2306 gram AgBr.
III. 0.1244 gram substance gave 0.1419 gram AgBr.

	Calculated for $C_6H_4Br_2O_4$.	Found. I.	II.	III.
Br	50.29	48.61	48.85	48.54

This body is readily soluble in water or alcohol with apparent decomposition, more sparingly soluble in ether, and insoluble in chloroform, ligroin, or benzol. The purified substance decomposes slowly on standing, and is still more unstable in solution. The decomposition of the solid becomes more rapid at higher temperature, and at about 200° it is immediate.

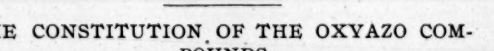
Action of Baric Hydrate on γ-Dibromide.

Although the γ-dibromide could not be obtained in a pure condition our analyses made it evident that it was the main constituent of the product which we had prepared; we therefore thought it worth while to try its behavior with baric hydrate. We have satisfied ourselves that no baric pyromucate is formed in the reaction, but we have not yet been able to study the products of the decomposition in detail. When 2.5 molecules of baric hydrate were added to an aqueous solution of the substance a precipitate was formed at once, and in a short time the solution gave a neutral reaction. The barium salt which separated proved to contain baric carbonate in abundance, but a considerable portion of it was soluble in boiling water. The acid set free from this salt could be extracted by ether, but remained as an uncrystallizable syrup on evaporation of the ether. The only soluble barium salt formed in the reaction appeared to be baric bromide, and no trace of pyromucic acid could be detected.

THE CONSTITUTION OF THE OXYAZO COMPOUNDS.

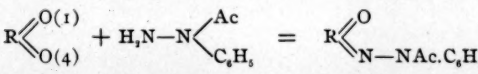
By William McPherson and Herbert C. Gore.

In a previous article published in this Journal[1] results were given which absolutely proved the constitution of the acyl derivatives of the paraoxyazo compounds. The problem was to decide between the two possible formulæ:



[1] Vol. 22, 364.

The proof was found in the synthesis of bodies having beyond doubt the constitution represented by Formula I. This synthesis was effected by the interaction of unsymmetrical acylphenylhydrazines and paraquinones according to the general reaction :



On comparing these hydrazone derivatives with the same derivatives of the corresponding oxyazo bodies, they were found to be not identical but isomeric. Hence the constitution of the acyl derivatives of the paraoxyazo bodies must be expressed by Formula II. In other words, they are true oxyazo compounds containing the acyl group joined to oxygen.

While this proof does not fix the constitution of the free oxyazo compounds, nevertheless the reactions bear indirectly upon the subject, and certain reasons were given for considering them, as well as their salts, true oxyazo bodies. One of these reasons, *viz.*, that the free paraoxyazo bodies cannot be quinone derivatives since they do not react with phenylhydrazine, must, however, be withdrawn, as I have found that under certain conditions a reaction does take place.[1] This reaction is being studied and it is hoped that it may throw some light on the constitution of these bodies.

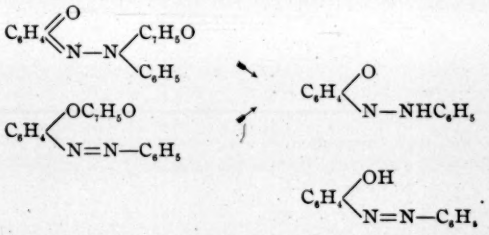
Since the above-mentioned article was published, Farmer and Hantzsch[2] have published the results of the measurements of the electrical conductivity of oxyazobenzene as well as of its sodium salt, and conclude that while the latter is a true oxyazo body the former is benzoquinonephenylhydrazone. The publication of these results was soon followed by an article by Auwers,[3] giving the results of cryoscopic measurements, which he believes prove that the paraoxyazo compounds are, in a free state, true oxyazo bodies, although the orthooxyazo compounds are quinone hydrazones. More recently Möhlau and Kegel,[4] from a study of the con-

[1] See note, this Journal, Vol. 25, 80.
[2] Ber. d. chem. Ges., 32, 3089.
[3] *Ibid.*, 33, 1302.
[4] *Ibid.*, 33, 2858.

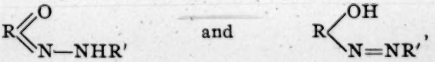
densation-products of certain paraoxyazo bodies with tetramethyldiamidobenzhydrol, conclude that the view of Farmer and Hantzsch is correct.

It will be noted that it is only the constitution of the free paraoxyazo compounds which remains unsettled. It is generally accepted that the salts, as well as the acyl and alkyl derivatives of these, are true oxyazo bodies. In the case of the members of the ortho series, all evidence goes to show that they are quinone hydrazones.

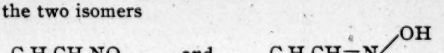
In the article[1] referred to above I have shown that both the acyl derivatives of the quinone hydrazones and their isomeric paraoxyazo derivatives give, on saponification, the same body. Thus quinone benzoylphenylhydrazone and its isomeric benzoyl derivative of oxyazobenzene give, on saponification with acids and alkalies, the same body; *viz.*, oxyazobenzene:



The investigation has been continued in the hope that some compound could be found which, on saponification, would give the two possible isomers



just as Hantzsch and Schultze[2] have been able to obtain from the sodium salt of phenylnitromethane by treatment with acids the two isomers



[1] This JOURNAL, **22**, 364.
[2] Ber. d. chem. Ges., **29**, 699.

Accordingly, the action of the unsymmetrical benzoyl-α-naphthylhydrazine on the paraquinones has been studied; and while the saponification of these has not led to the isolation of such isomeric bodies, yet the results are of sufficient interest to make their publication desirable. They show that the acyl derivatives of the paraoxyazo bodies formed by the interaction of α-naphthyl diazonium chloride on phenol, orthocresol, and thymol, respectively, contain the acyl group joined to oxygen and hence are true oxyazo compounds.

EXPERIMENTAL PART.

I. The Preparation of α-Benzoyl-α-Naphthylhydrazine, $C_{10}H_7.NC_7H_5O.NH_2$.

This compound was prepared according to Widman's method[1] for the preparation of unsymmetrical hydrazines. To 1 gram of β-acetylnaphthylhydrazine (m. p. 143°) dissolved in 10 cc. of benzene was added the theoretical amount of benzoyl chloride. The flask was connected with a return condenser and the solution boiled until the evolution of hydrochloric acid ceased. This required about one hour. On evaporating the benzene, a thick, gummy liquid remained, which was dissolved in as little alcohol as possible. On scratching the sides of the beaker containing the solution with a glass rod, white crystals of α-benzoyl-β-acetyl-α-naphthylhydrazine separated. Yield, 0.84 gram. By further crystallization from alcohol the pure body, melting at 184°, was obtained.

0.2046 gram substance gave 0.5603 gram CO_2; and 0.0967 gram H_2O.

0.2062 gram substance gave 0.1017 gram H_2O.

0.3010 gram substance gave 26.5 cc. N at 25° and 741 mm.

	Calculated for $C_{19}H_{16}N_2O_2$.	Found. I.	Found. II.
C	75.00	74.69	....
H	5.26	5.25	5.48
N	9.21	9.62	....

[1] Monograph—"Ueber asymmetrische Secundäre Phenylhydrazine" published by the "Gesellschaft der Wissenschaften" at Upsala, 1893; also Ber. d. chem Ges., **26**, 945.

The pure compound is fairly soluble in hot alcohol, from which it is deposited in large, lath-shaped crystals. It is slightly soluble in benzene and benzene-ligroin, being deposited from the latter in little nodules of microscopic crystals. By treatment with dilute sulphuric acid it is converted into α-benzoyl-α-naphthylhydrazine. To effect this change a solution of 2 cc. of sulphuric acid, in 15 cc. of water, was added to 2 grams of the hydrazine. The mixture was heated and sufficient alcohol added to form a clear solution. The flask was then connected with a return condenser and the contents kept at a boiling temperature for about four hours, or until the odor of benzoic ether was detected. The cooled solution was then neutralized with sodium carbonate and extracted with ether, which, on evaporation, deposited white crystals of the unsymmetrical benzoyl-α-naphthylhydrazine. By repeated crystallization from alcohol the pure body melting at 120°.5 was obtained:

0.2058 gram substance gave 0.5854 gram CO_2; and 0.1070 gram H_2O.

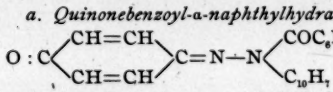
0.2032 gram substance gave 20 cc. N at 23° and 744.3 mm.

	Calculated for $C_{17}H_{14}N_2O$.	Found.
C	77.86	77.58
H	5.34	5.77
N	10.68	10.91

α-Benzoylnaphthylhydrazine is very soluble in alcohol and benzene. It is deposited from its alcoholic solution in large truncated pyramids. On addition of ligroin to its benzene solution, feathery crystals, melting at 98°, are deposited. On gentle heating or on long standing in a vacuum the melting-point gradually rises to 120°.5.

II. The Action of α-Benzoyl-α-naphthylhydrazine on Paraquinones of the Benzene Series.

a. Quinonebenzoyl-α-naphthylhydrazone,



.—A solution of 1 gram of benzoquinone in 15 cc. of alcohol was poured into 500 cc. of water. To this was added 2 grams of α-benzoyl-α-naph-

thylhydrazine dissolved in 200 cc. of water and 50 cc. of alcohol. The addition of a few drops of hydrochloric acid accelerates the reaction. The yellow hydrazone at once began to separate. After half an hour the precipitate was collected by stirring, filtered off and dried on a clay plate. 2.2 grams of the impure body were obtained. The hydrazone is difficult to purify on account of its tendency to separate from its solution in the form of an oil. It is very soluble in benzene, alcohol, ether, and chloroform, separating from each as an oil that does not solidify. On heating the oil with successive portions of ligroin, however, a solution was obtained from which the hydrazone was deposited as a crust on the sides of the beaker. On standing for two or three days a few large crystals were formed which were removed and washed with ligroin. By further purification from ligroin a small amount of the body was obtained in masses of plates, melting sharply at 113°.5.

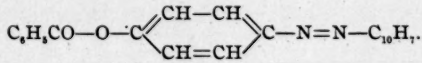
0.2238 gram substance gave 0.6484 gram CO_2; and 0.0961 gram H_2O.

0.2258 gram substance gave 17.6 cc. N at 31°.5 and 738.8 mm.

	Calculated for $C_{28}H_{16}N_2O_2$.	Found.
C	78.41	79.015
H	4.54	4.77
N	7.95	8.22

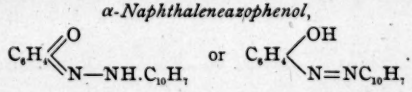
The percentage of carbon found is too high, but the difficulty experienced in obtaining the pure material prevented our making another combustion.

Quinone benzoyl-α-naphthylhydrazone is isomeric with the benzoyl derivative of α-naphthaleneazophenol. The latter must therefore have the formula :



On saponification both of these compounds yield the same body, *viz.* :

α-Naphthaleneazophenol,



This compound can be readily prepared by the interaction of α-naphthyl diazonium chloride and phenol. 7.7 grams of α-naphthylamine were ground in a mortar with a hydrochloric acid solution corresponding to 3.9 grams of the anhydrous acid. The resulting product was added to 200 cc. of water, cooled to 5°, and diazotized with the required amount of sodium nitrite dissolved in 100 cc. of water. The solution was then filtered and added to a cold solution of sodium phenolate, prepared by adding 5 grams of phenol and 2.4 grams of sodium hydroxide to a liter of water. After standing twenty-four hours the azo compound was precipitated by hydrochloric acid and purified by repeated crystallization from benzene-ligroin (m. p. 136°).

0.2016 gram substance gave 0.5708 gram CO_2; and 0.0954 gram H_2O.

0.2062 gram substance gave 0.0944 gram H_2O.

0.2045 gram substance gave 21.8 cc. N at 26°.5 and 740.8 mm.

	Calculated for $C_{16}H_{12}N_2O$.	Found. I.	II.
C	77.42	77.22	....
H	4.84	5.26	5.09
N	11.29	11.56	....

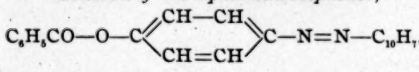
α-Naphthaleneazophenol is easily soluble in alcohol, separating in little clumps of brownish needles. From benzene it separates in yellowish needles. It is slightly soluble in ligroin, separating in brownish plates. When these are heated to 130° the color suddenly changes to red. This red modification is deposited from its ligroin solution in the form of reddish silky needles. The distinction between the two modifications is thus very marked. The experiments of Hewitt[1] pointed to the presence of water in the brown body; but experiments showed that the change from the brown to the red modification was not attended by any change in weight. It is possible that we have here the two isomers

$$C_{10}H_7N=N—C_6H_4OH \text{ and } C_{10}H_7NH—N=C_6H_4=O,$$

but no evidence could be obtained of any difference in chemical behavior.

[1] Ber. d. chem. Ges., 28, 799.

Benzoate of α-Naphthaleneazophenol,



This compound was readily obtained from naphthaleneazophenol by means of Baumann's reaction. By precipitating its benzene solution with ligroin, the pure body was obtained melting at 120°.

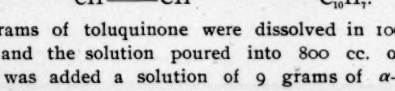
0.2015 gram substance gave 0.5801 gram CO_2; and 0.0794 gram H_2O.

0.2154 gram substance gave 16.35 cc. N at 29° and 749.8 mm.

	Calculated for $C_{23}H_{16}N_2O_2$.	Found.
C	78.41	78.515
H	4.54	4.38
N	7.95	8.23

The compound is readily soluble in chloroform and benzene and fairly so in ether and alcohol. It is deposited in the form of needles from its solution in each of these solvents.

b. Toluquinonebenzoyl-α-naphthylhydrazone,



3.8 grams of toluquinone were dissolved in 100 cc. of alcohol and the solution poured into 800 cc. of water. To this was added a solution of 9 grams of α-benzoyl-α-naphthylhydrazine hydrochloride dissolved in 400 cc. of dilute alcohol (equal volumes of alcohol and water). The resulting mixture was allowed to stand over night when the hydrazone was collected by stirring and removed by filtration. (Yield of impure compound 8.5 grams.) Like the corresponding derivative of benzoquinone, the impure compound is deposited from the common solvents as an oil. It was finally obtained in the form of crystals by repeated treatment with small amounts of hot methyl alcohol, which dissolved principally the resinous matter. The residue left was bright-yellow. This was then deposited from benzene-ligroin in clusters of stellar crystals. The pure compound melts at 166°.

0.2012 gram substance gave 0.5812 gram CO_2; and 0.0953 gram H_2O.

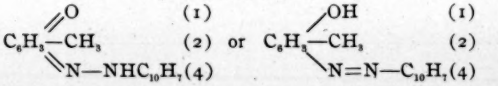
0.2509 gram substance gave 17.8 cc. N at 19°.5 and 737.3 mm.

	Calculated for $C_{24}H_{18}N_2O_2$.	Found.
C	78.69	78.78
H	4.91	5.26
N	7.65	7.92

From alcohol the pure hydrazone crystallizes either in broad prismatic crystals with pyramidal ends or in squares.

The compound is not identical but isomeric with the benzoate of α-naphthaleneazoorthocresol. The latter must therefore be a true oxyazo compound containing the benzoyl group joined to oxygen. Both of these compounds yield, on saponification,

α-Naphthaleneazoorthocresol,



This compound can be readily prepared by the interaction of α-naphthyl diazonium chloride and orthocresol. The following conditions were found by Mr. C. P. Linville, of this laboratory, to give good results: 10.5 grams of α-naphthylamine were triturated in a mortar with a solution of hydrochloric acid containing 5.36 grams of the anhydrous acid. 350 cc. of water were added and the compound diazotized at 5° by the addition of a cold solution of 5.5 grams of sodium nitrite in 100 cc. of water. The resulting diazonaphthalene solution, filtered from the residue, was gradually added to a cold solution of 8 grams of orthocresol and 3 grams of sodium hydroxide in 1500 cc. of water. The α-naphthaleneazocresol separated as a yellow precipitate. Yield of crude product 12 grams. It can easily be purified by benzene-ligroin. Melting-point 154°.5.

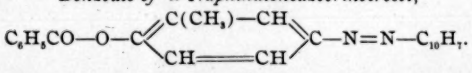
0.2000 gram substance gave 0.5713 gram CO_2; and 0.1018 gram H_2O.

0.2000 gram substance gave 19.2 cc. N at 20° and 744 mm.

	Calculated for $C_{17}H_{14}N_2O$.	Found.
C	77.86	77.90
H	5.34	5.65
N	10.68	10.79

The compound is very soluble in alcohol and benzene. From the latter it separates in reddish-yellow needles and ball-shaped masses.

Benzoate of α-Naphthaleneazoorthocresol,



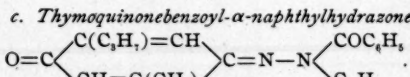
To obtain this the α-naphthaleneazocresol was dissolved in a 10 per cent solution of sodium hydroxide and the resulting solution shaken up with a slight excess of benzoyl chloride. The compound was purified by crystallization, first from alcohol and then from ligroin, from which it separates in long, thin, flat needles. Melting-point 120°.

0.2000 gram substance gave 0.5763 gram CO_2; and 0.0943 gram H_2O.

0.2000 gram substance gave 14.6 cc. N at 25° and 743 mm.

	Calculated for $C_{24}H_{18}N_2O_2$.	Found.
C	78.68	78.58
H	4.92	5.24
N	7.65	8.005

c. Thymoquinonebenzoyl-α-naphthylhydrazone,



3.13 grams of thymoquinone were dissolved in 200 cc. of alcohol and the solution poured into 400 cc. of cold water. To this was added a solution of 5 grams of α-benzoyl-α-naphthylhydrazine hydrochloride in 320 cc. of dilute alcohol (equal parts of alcohol and water). After standing for twenty-four hours, the hydrazone separated in beautiful yellow crystalline groups. Yield 5 grams. On crystallizing from benzene-ligroin the pure body was obtained, melting at 151°.5.

0.2009 gram substance gave 0.5860 gram CO_2; and 0.1095 gram H_2O.

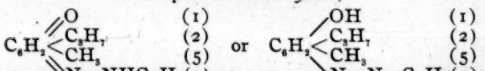
0.2605 gram substance gave 16.4 cc. N at 16°.5 and 728 mm.

	Calculated for $C_{17}H_{14}N_2O_2$.	Found.
C	79.41	79.55
H	5.88	6.06
N	6.86	7.04

The hydrazone crystallizes from alcohol in beautiful rhombohedral crystals and from benzene-ligroin in compact bladed aggregates.

Thymoquinone benzoyl-α-naphthylhydrazone, on saponification, yields α-naphthaleneazothymol. On benzoylating this body, however, we obtain not the original hydrazone but the isomeric benzoate of α-naphthaleneazothymol, which body must therefore contain the benzoyl group joined to oxygen.

α-Naphthaleneazothymol,[1]



The α-naphthaleneazothymol so prepared is identical with that obtained by the ordinary method of preparing oxyazo bodies. Mr. W. L. Dubois, of this laboratory, obtained a yield of 78 per cent under the following conditions: 7.7 grams of finely powdered α-naphthylamine were suspended in 200 cc. of water, to which had been added a solution of hydrochloric acid corresponding to 3.9 grams of the anhydrous acid. This was cooled, diazotized with sodium nitrite, filtered, and the resulting solution of the α-naphthyl diazonium chloride added slowly to a cold solution of 8.07 grams of thymol and 2.6 grams of sodium hydroxide in 1000 cc. of water. The yellowish-brown α-naphthaleneazothymol separated as fast as ormed. From benzene-ligroin it separates in monoclinic crystals melting at 117°.5.

0.2009 gram substance gave 0.5820 gram CO_2; and 0.1246 gram H_2O.

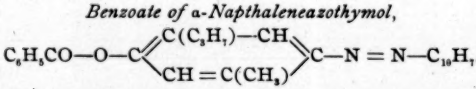
0.2005 gram substance gave 16.9 cc. N at 23° and 740 mm.

[1] The melting-point of the corresponding benzeneazothymol is given by Mazzara and Possetto (Gazz. chim. ital., 15, 52–228) as 85° to 90°. The melting-point is not raised above this by repeated crystallization from alcohol. By a single crystallization from benzene, however, the melting-point is raised to 109° and remains constant.

	Calculated for $C_{20}H_{20}N_2O$.	Found.
C	78.95	79.01
H	6.58	6.89
N	9.21	9.295

The compound is very soluble in ether and benzene and fairly so in alcohol.

Benzoate of α-Napthaleneazothymol,



This compound is obtained from α-naphthaleneazothymol by Baumann's reaction. It is best purified by crystallizing first from benzene-ligroin and finally from alcohol. Melting-point 173°.5. The melting-point is not raised above 170° by crystallization from benzene-ligroin alone.

0.1823 gram substance gave 0.5312 gram CO_2; and 0.1026 gram H_2O.

0.2500 gram substance gave 16.3 cc. N at 28° and 743 mm.

	Calculated for $C_{27}H_{24}N_2O_2$.	Found.
C	79.41	79.47
H	5.88	6.25
N	6.86	7.066

The compound is readily soluble in ether and benzene, less so in ligroin, and with difficulty in alcohol. From benzene and alcohol it crystallizes in needles. On saponification it yields α-naphthaleneazothymol.

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OHIO STATE UNIVERSITY.

ACTION OF PHENOLS ON ETHYLIC OXALATE.

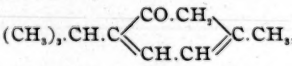
BY J. BISHOP TINGLE AND LEO O'BYRNE.

Theoretical.

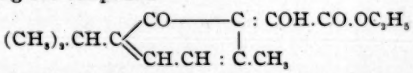
In the course of a paper on camphoroxalic acid derivatives by one of the present writers and Alfred Tingle,[1] a description was given of an experiment on the interaction of ethylic oxalate and thymol, in the presence of sodium. The product was obtained in the form of an oil, and gave a dark-red color-

[1] This JOURNAL, 21, 261 (1899).

ation with alcohol and ferric chloride. The most obvious explanation of the condensation is that the thymol had reacted in its secondary form



producing the compound



We thought that it might be interesting to examine the matter more closely, and we have accordingly tested the behavior, under similar circumstances, of a number of phenols and allied compounds. The results given in the present paper are only to be regarded as preliminary, but, as the work will suffer interruption for a time, it appears desirable to place our observations on record. In addition to thymol the following compounds were investigated: pyrocatechol, carvacrol, picric acid, β-naphthol, ethylic salicylate, quinone, guaiacol, resorcinol, phloroglucinol, hydroquinol, anisoïl, and carvol. Of these the first six showed no sign of having reacted. Guaiacol yielded tarry products which could not be investigated. Anisoïl and carvol, as was to be anticipated from their constitution, yielded condensation-products of the desired kind. Resorcinol, phloroglucinol, and hydroquinol also yielded compounds. That from the first melted and decomposed at 257°–258°, and is possibly identical with the substance which Michael[1] obtained by the interaction of resorcinol, ethylic oxalate, and dry sodium ethoxide at 200°. It gives a red coloration with ferric chloride and alcohol. The compound from phloroglucinol also gives a reddish color with ferric chloride and alcohol. It is incompletely melted at 305°, and may possibly prove to be an oxidation-product of the phenol. Hydroquinol yielded a substance which was somewhat difficult to purify. It blackened above 200°, was not melted at 300°, and gave no coloration with alcohol and ferric chloride. It is very probable that this compound also is formed as the result of oxidation.

[1] J. prakt. Chem., [2], 35, 510.

Experimental.

In all cases, unless otherwise stated, the experiments were performed in the following manner: ethylic oxalate and the phenol, or other compound, were mixed in equidecigram molecular proportion, light petroleum (300 cc.), which had been thoroughly dried, was added, then an atomic proportion of sodium wire. The flask containing the mixture was connected to a reflux condenser, and, if needful, heated on the water-bath. After the sodium had dissolved, the flask, suitably protected from moisture, was allowed to remain at the ordinary temperature during about twenty hours; the contents were then poured into water, the light petroleum removed, and the aqueous liquid extracted two or three times with ether; this was removed, an excess of dilute sulphuric acid added to the aqueous solution, and the extraction with ether repeated several times. The light petroleum and ether extracts were dried by means of calcium chloride, and distilled from the water-bath. For the sake of brevity, the combined ethereal extracts, before acidification of the aqueous liquid, will be termed in the following pages "ethereal extract 1," while the combination of those made after the addition of acid will be referred to as "ethereal extract 2."

Pyrocatechol.—On account of the sparing solubility of this compound in light petroleum, absolute alcohol was employed in its place. The sodium was first dissolved in the alcohol, then the other two ingredients added. The subsequent procedure was exactly that described above. From neither of the ethereal extracts was anything but pyrocatechol recovered.

Carvacrol.—The experiment was carried out in the usual manner. The light petroleum extract consisted of an oil which proved to be carvacrol. The ethereal extract 2 showed signs of crystallization (oxalic acid?) but contained carvacrol; as it is probable that any condensation-compound (ethylic salt) would crystallize with much greater difficulty than the free acid, corresponding with camphoroxalic acid, the substance was hydrolyzed and the product purified, but no new compound could be detected.

Picric Acid.—This experiment was carried out in exactly the same manner as that with pyrocatechol, and gave a similarly negative result.

β-Naphthol.—This substance behaved like carvacrol in all respects. The ethereal extract 2 was tarry, melted at about 160°, and was not further investigated.

Ethylic Salicylate.—The modification of E. Fischer's method, which has been previously described by one of us and Alfred Tingle,[1] was advantageously employed for the preparation of this compound. Salicylic acid (50 grams) was mixed with 95 per cent alcohol (300 cc.) and concentrated sulphuric acid (15 cc.), and boiled in a reflux apparatus during seven hours. The greater portion of the alcohol was removed on the water-bath, the residue neutralized with sodium hydrogen carbonate, dissolved in water, and extracted with ether. The yield is excellent, but is improved by the use of a pressure bottle.[2] With this appliance, salicylic acid (40 grams), 95 per cent alcohol (150 cc.), and concentrated sulphuric acid (24 cc.), after being heated at 100° during four hours, yielded 40 grams of ethylic salicylate and 5.9 grams unchanged acid. In another experiment the alcohol and sulphuric acid were reduced to 100 cc. and 16 cc. respectively, without any special effect on the yield, the other conditions remaining unchanged; the chief factor of importance is apparently to keep the proportion of sulphuric acid somewhat high. No new compound could be isolated by treating ethylic salicylate with ethylic oxalate and sodium in the ordinary manner, a result fully in accordance with expectation.

Quinone.—In order to dissolve the sodium in this case, it was necessary to add about 200 cc. absolute alcohol to the light petroleum; the mixture immediately turned black. The subsequent working of the product was attended with difficulty on account of the formation of emulsions. The result was similar when sodium ethoxide, dissolved in absolute alcohol, was substituted for the sodium and light petroleum.

Guaiacol.—Gave entirely negative results.

[1] This JOURNAL, **21**, 255 (1899).

[2] We are indebted for these details to Dr. A. Tingle, of Columbia University, New York.

Resorcinol.—In order to obtain a solution of the sodium it was necessary to add absolute alcohol (150 cc.) to the solution of the materials in light petroleum. The ethereal extract 1 deposited resorcinol, melting at 110° to 111°. The ethereal extract 2 yielded yellow crystals which, after purification by means of alcohol, melted and decomposed at 257°–258°. The compound darkens below its melting-point, is very readily soluble in alcohol, and the solution gives a red coloration with ferric chloride. It is hoped that light may be thrown on the nature of this compound by its subsequent investigation.

Phloroglucinol.—As in the case of resorcinol, it was necessary to add absolute alcohol in order to cause solution of the sodium. The ethereal extract 1 deposited a compound which crystallized from alcohol in colorless plates and remained unmelted at 240°; somewhat below this temperature it blackened. No coloration was produced with alcohol and ferric chloride. Ethereal extract 2 also deposited crystals which were purified like the others. They softened, but did not melt, at 305° and gave a reddish coloration with alcohol and ferric chloride.

Hydroquinol.—The sodium remained practically unattacked after heating for some time, a little benzene was therefore added, but this only caused the formation of a brown crust on the metal. Then absolute alcohol (100 cc.) was poured in, whereupon the mixture immediately blackened. The ethereal extract 1 apparently only contained unchanged phenol. The ethereal extract 2 did not change with alcohol and ferric chloride. It was digested with sodium hydroxide, acidified, and digested with sodium carbonate solution to separate any acid from phenol; as the solution was quite clear it was acidified, and the black precipitate removed and dried. Extraction of it by means of alcohol and benzene left a tarry mass, which was not further investigated, and a white solid; this blackened above 200°, but remained unmelted at 300°.

Anisoïl.—This also required the addition of absolute alcohol (100 cc.) to dissolve the sodium. The light petroleum gave no residue. The ethereal extract 1 yielded an oil which gave no color with ferric chloride and alcohol. The ethereal

extract 2 was oily but gave a deep-red coloration with ferric chloride and alcohol, showing that the desired condensation had taken place.

Carvol.—This reacts readily in light petroleum solution. The product was obtained from both the ethereal extracts as well as from the light petroleum. The new compound gives a deep-red coloration with ferric chloride and alcohol and is oily. After hydrolysis an oil was also obtained which forms a barium and copper salt, but they are difficult to purify and, like the parent substance, readily become resinous. The resin has a strong odor of violets.

The work will be continued and extended in various directions.

LEWIS INSTITUTE, CHICAGO, ILL.

Contribution from the North Carolina Experiment Station.

THE DETERMINATION OF PENTOSANS.

BY G. S. FRAPS.

The term "pentosan" is applied to those substances occurring in vegetable materials which yield furfural when distilled with hydrochloric acid, though their nature is a problem as yet unsolved. The method of determining pentosans consists in distilling the substance with hydrochloric acid of 1.06 sp. gr., and precipitating the furfural in the distillate with phloroglucol. It is assumed that the only product in the distillate which is precipitated by phloroglucol is furfural, but this is not the case. As already pointed out by the writer,[1] small quantities of insoluble fatty acids pass over into the distillate, which, while not precipitated by furfural, appear in the distillate unless previously filtered out. Further, if the distillate is allowed to stand ten or more hours, very often an amorphous black precipitate separates, which would also appear in the distillate, either as such or combined with the phloroglucol, since the vessel is always allowed to stand over night after adding the precipitating agent. Finally, the distillate always contains one or more substances which do not appear to be furfural, and which are precipitated by phloro-

[1] Bull. 172, 56, North Carolina Experiment Station.

glucol. These substances will be discussed in the following pages.

Furaloid.

While carrying through the determination of pentosans in a number of materials, the possibility that the distillation with hydrochloric acid might destroy some of the furfural occurred to the writer. This possibility seemed stronger than when one of the distillates was evaporated and found to leave a brown residue. To test the point further, corn bran was distilled with hydrochloric acid in the usual way for the determination of pentosans, and the distillate divided into two equal portions. One portion was made up to 500 cc. with acid, and precipitated with phloroglucol. The second portion (200 cc.) was placed in a distilling flask and 170 cc. distilled. The distillate was returned to the flask, distilled to a small volume, 30 cc. acid added, distilled, and the addition of acid and distillation repeated once more. The distillate was made up once to 500 cc., and the furfural precipitated with phloroglucol. The weights of the precipitates were, from:

	Gram.
Undistilled portion	0.2216
Distilled portion	0.1715
Loss	0.0501
Loss, per cent	22.5

Other experiments gave the same result, though the loss was not so great, as the second distillation was never carried out twice.

The question arose, is this loss due to oxidation during the second distillation? That it was not is shown by the fact that the loss was as great when the distillation took place in a current of carbon dioxide as in the air. In performing this experiment, the distillate was divided into several portions, and two portions precipitated directly, after dilution to 500 cc. with hydrochloric acid of 1.06 sp. gr. The other portions were placed in distilling flasks and distilled almost completely, then 30 cc. of acid were added, and distilled. The addition of acid and distillation was repeated several times,

the distillate then made up to 500 cc., and precipitated as before. This is the method used in all subsequent experiments, unless otherwise noted.

Timothy hay was the material used. The weights of the precipitates were, from :

	I. Gram.	II. Gram.
Undistilled portions	0.2763	0.2767
Distilled alone	0.2299	....
Loss, per cent	16.8	....
	Gram.	Gram.
Distilled with CO_2	0.2216	0.2236
Loss, per cent	19.1	19.8

The loss was not caused by oxidation during the second distillation.

Is this loss due to decomposition of furfural? was the next question. To test this point, freshly prepared furfural was dissolved in hydrochloric acid of 1.06 sp. gr., and portions distilled as in the preceding experiment. The precipitates weighed, from :

	Gram.	Gram.
Undistilled portions	0.2815	0.2805
Distilled portions	0.2804	....
Loss	none	....

After standing four days the solution of furfural became brown, probably by oxidation. In this condition it gave the following results :

	Gram.	Gram.	Gram.
Undistilled portions	0.2880	0.2863	.....
Distilled portions	0.2785	0.2779	0.2762
Mean loss			0.0096
Loss, per cent			3.2

The error of analysis may be 0.0030 on each precipitate, so that the loss is very small.

The possibility still remained that during the first distillation of the substance with hydrochloric acid the furfural

formed is changed, by oxidation or otherwise, so that it does not pass over during the second distillation. To test this possibility, a solution of the furfural was prepared and distilled in the usual way. One portion of the distillate was distilled as before, and a second portion precipitated directly. The results follow:

	Gram.
Distilled once	0.4577
Distilled twice	0.4510
Loss	0.0065
Loss, per cent	1.5

The loss is less than when the furfural solution had stood four days.

These experiments seem to show that when vegetable materials are distilled with hydrochloric acid there may be formed, besides furfural, a substance or substances which precipitates phloroglucol, and is destroyed (in part or wholly) by a second distillation. Until more is learned as to the nature of this substance, for convenience's sake, I shall use the term furaloid to designate it.

Occurrence of Furaloid-yielding Substances.

The furaloid-yielding substances were determined in the manner already noted, namely, the material was distilled with hydrochloric acid, the distillate divided into two portions, and one portion distilled again. The percentage lost was assumed to represent the percentage of furaloids present in the crude furfural. This method is not supposed to be very accurate, but only to give some idea as to the occurrence of these substances.

The furaloid-yielding substances are widely distributed in nature as all the materials tested contained them. The table shows the percentage obtained by the method just described.

Furaloid in Crude Furfural.

	Weight lost. Gram.	Per cent lost (furaloid).
Cottonseed meal	0.0301	7.4
Cowpea meal	0.0197	17.9
Crimson clover hay	0.0337	11.7
Irish potato vines	0.0278	10.2
Corn bran	0.0501	22.6
Timothy hay	0.0596	18.1
Pine straw	0.0241	13.2
Gum arabic	0.0338	12.9
Corn cobs	0.0595	10.1
Okra hulls	0.0513	11.5
Oak sawdust	0.0311	6.9
Oxycellulose	0.0148	13.8

None of these losses are small enough to be ascribed entirely to change in furfural. In the table the distillates from the materials down to pine straw were allowed to stand over night and filtered before being distilled. The distillates from pine straw and the others were redistilled the same day as prepared. The oxycellulose was prepared by oxidizing filter-paper with chromic acid in the presence of sulphuric acid.

In some cases the residue in the flask was evaporated to dryness in a platinum dish, dried, weighed, ignited, and weighed again. The organic matter so determined was, as a rule, about 50 per cent of the loss in weight of the phloroglucid precipitate, but it varied considerably. On account of this variation, as it is not certain that the furaloid was changed to non-volatile substances, little value was attached to these figures, and they are not given.

Distribution of Furaloid-yielding Substances.

When substances containing pentosans are boiled with 1.25 per cent sulphuric acid, and then with 1.25 per cent caustic soda, as for the determination of crude fiber, part of the pentosans is dissolved by the acid, part by the alkali, and usually a part remains in the crude fiber.

In order to ascertain to what extent the furaloid-yielding bodies were dissolved by 1.25 per cent sulphuric acid, 10 grams of the material were boiled for half an hour with a liter

of the acid, filtered, and washed. The residue was distilled with hydrochloric acid and furaloid determined in the distillate. The filtrate was neutralized with barium carbonate, filtered, evaporated to a small volume, and distilled with hydrochloric acid. Furaloid was determined in the distillate. Furfural was given off during the evaporation.

Furaloid in Crude Furfural.

	Entire material. Per cent.	Dissolved by acid. Per cent.	Undissolved. Per cent.
Corn bran	22.6	0.0	6
Timothy hay	18.1	7.3	2
Crimson clover hay	11.7	7.0	1

The furfuraloid-yielding substances were almost completely dissolved by the acid and at the same time destroyed entirely, or to a great extent.

About 90 per cent of the pentosans in the corn bran and 45 per cent of those in the timothy hay were dissolved by the acid.

Digestibility of the Furaloid-yielding Substances.

One experiment was made to see if the furaloid-yielding bodies were more or less digested than the pentosans. The furaloids were determined in the distillate from the excrement from a sheep fed timothy hay, which had been used in digestion experiments.

	Per cent.
Pentosans digested in hay	55.9
Furaloids in crude furfural from hay	18.1
" " furfural from excrement	10.7

The furaloid-yielding bodies have disappeared to a greater extent than the pentosans and must be digested. From the above figures their digestibility is about 75 per cent compared with 60 per cent for that of the pentosans.

Determination of Pentosans.

It appeared possible that the substances here called furaloids were formed from the true pentosans (anhydrides of pentose sugars) by distillation with hydrochloric acid, and their presence did not affect the pentosan determination. The

contrary seems to be true. To test this point, a pentose sugar was prepared and tested in the following way: Finely-ground corn cobs were extracted with dilute ammonia and hydrolyzed with dilute hydrochloric acid. The acid was neutralized with lead carbonate, the liquid evaporated to a small volume, two volumes of alcohol added and filtered. The filtrate was evaporated to a small volume, and xylose No. 1 precipitated with absolute alcohol. The alcohol was partly evaporated, water added, and the solution saturated in the cold with barium hydroxide. The impure barium compound of the sugars was precipitated by adding alcohol (xylose No. 2). Both of these materials were impure, but sufficiently pure for the end in view.

They were distilled with hydrochloric acid and furaloid determined in the crude furfural of the distillate. The weights of the precipitates were:

	Xylose No. 1.		Xylose No. 2.	
	Gram.	Gram.	Gram.	Gram.
Undistilled	0.1555	0.1594	0.0257	0.0250
Distilled	0.1524	0.1530	0.0257	0.0240
Loss, per cent	2	4	0	0

With these figures may be compared those obtained from the products of the hydrolysis of corn bran, timothy hay, and crimson clover hay. In detail these were:

	Bran. Gram.	Timothy hay. Gram.	Crimson clover hay. Gram.
Undistilled	0.5025	0.2891	0.0829
Distilled	0.5025	0.2680	0.0772
Loss	0.0000	0.0110	0.0057
Loss, per cent	0	7.3	7.0

Allowing for error of analysis the differences are small. It seems probable that furaloids are not formed by distilling pentose sugars with hydrochloric acid. Accepting this as true, it is evident that the presence of furaloids in the crude furfural affects the determination of the pentoses. Until we know more about the pentosans, and the furaloid-yielding substances, it is questionable whether it would be expedient to determine them separately, since they can very conve-

niently be grouped together. A method of separating the furaloid from the crude furfural was tested, as follows: The vegetable material was heated two hours under a reflux condenser with hydrochloric acid, instead of distilling off directly. The condenser was then turned down and the furfural distilled as usual. A brown substance was deposited in the tube of the condenser. Furaloids were determined in the distillate and found to be: Timothy hay, 1 per cent; okra hulls, 5 per cent; excrement, 3 per cent; corn silage, 14 per cent. The furaloids were destroyed, except in the case of the silage. It is feared that this method would give too low results for furfural.

Summary.

The distillate from vegetable materials with hydrochloric acid may contain, besides other things, fatty acids, a substance which separates as a black precipitate if the vessel is allowed to stand, and a substance or substances which is destroyed by distilling again (furaloid). All three of these may appear in the phloroglucol precipitate.

The furaloid-yielding bodies were found in all the materials tested, the crude furfural in the hydrochloric acid distillate containing from 7 to 23 per cent furaloid.

The furaloid-yielding bodies are hydrolyzed by boiling 1.25 per cent sulphuric acid, and lost in the subsequent evaporation. They are digested to a greater extent than the total pentosans in the one sample of timothy hay excrement tested.

The furaloid is not formed by the action of the hydrochloric acid on pentose sugars.

The work above described was done in the laboratory of the North Carolina Experiment Station, with the permission of Prof. W. A. Withers, chemist.

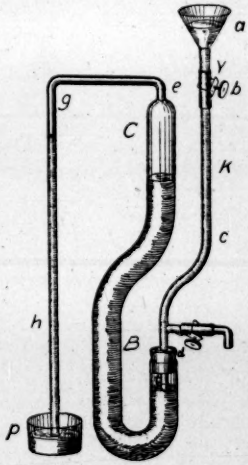
AN EASILY CONSTRUCTED BAROMETER.

By George W. Russell.

The necessity of a barometer in every chemical and physical laboratory, and the refusal of a prominent dealer to guarantee the safe arrival of the convenient Bunsen, or siphon, form

make desirable some simple and efficient means of filling this piece of apparatus, and the following device has been found to work well. As is well known, the boiling of a large quantity of mercury in straight glass tubes, except under diminished pressure, is troublesome and dangerous, and in the siphon tubes it is almost impossible.

By the method here described, so diminished a pressure over the top of the column of mercury can be maintained that all air and water vapor, except the smallest trace, can be gotten rid of, and a barometer obtained sufficient for all but the most exacting gas analyses, and any one who can seal two glass tubes together can make it. The cost is trifling. The error in measuring the height of the siphon barometer is ordinarily 0.1 mm., and this is much greater than the depression due to the vapor remaining in a tube filled as described in this note.



A tube B C of suitable diameter (say 8 to 10 mm.) and with walls of medium thickness is drawn out at *e* to a suitable capillary, and then bent into the siphon form. It is then covered with wax and graduated according to the well-known method of Bunsen, and etched with liquid hydrofluoric acid (the acid may be conveniently applied with a tuft of cotton fastened to the end of a platinum wire), cleaned with a hot solution of sulphuric acid and potassium bichromate, washed with distilled water, and thoroughly dried.

Now seal to BC, at *e*, a tube, *g h*, of about 0.6 mm. internal diameter and bent as shown, with *g h* about 800 mm. long. The tube *kct* is about 1 mm. internal diameter, bent as shown, and fitted into B C by a good cork. The apparatus is clamped in position and a train of U-tubes containing sulphuric acid is attached to *kct* at the rubber connection *y*, and air aspirated through the system till all water

vapor is removed, then the funnel *a* is attached and a small cup *h* containing mercury placed under the end of the tube *gh*. Mercury at a temperature of 105° to 120° is slowly filtered through the tube *kct* until the bend is filled 40 to 50 mm.; then close clamp *b* and open clamp *d* so that the mercury in the bend may rise above the end of *t*. Now close clamp *d*, open *b*, and slowly filter the hot mercury into the barometer tube, meanwhile carefully running a Bunsen flame up and down B C. After the tube is filled and the mercury runs over into *p*, open the clamp *d*, and allow the mercury to flow out at clamp *d* and fall in B C. The mercury can now be heated to boiling and kept at this temperature for some time, then close *d* and filter more mercury into B C till it fills the capillary and runs over into *p*. This process can be repeated indefinitely, but one repetition is usually sufficient. Before sealing off *e* it is best to allow the system to stand a day or so. Seal off the capillary at *e*, take out the cork and filling tube, and set up the barometer in the usual position.

In this way can be made, in the laboratory, an inexpensive barometer, and one sufficiently accurate for all ordinary experimental work of the student. The tubes can be bent and graduated as indicated or they can be purchased ready for drawing out and sealing to the capillary.

HIGH SCHOOL, ROANOKE, VA.,
March 13, 1901.

OBITUARY.

FRANÇOIS MARIE RAOULT.

With the death of Raoult in Grenoble, on April 1st, 1901, France has lost her most prominent physical chemist. The importance of the work of Raoult on the development of modern physical chemistry is not easily overestimated. He was the first to point out clearly, as the result of elaborate experimental investigations, the laws of the lowering of the vapor-tension and of the freezing-point of solvents by dissolved substances. He found that those substances which, in solution, conduct the current and are, therefore, known as electrolytes, give greater lowering of vapor-tension and of freezing-point than the non-electrolytes. We all know the importance of this discovery. It was to account for these facts, together with the greater osmotic pressure exerted by the electrolytes,

that Arrhenius proposed the theory of electrolytic dissociation. The work of Raoult on lowering of freezing-point and lowering of vapor-tension, together with that of Pfeffer on osmotic pressure, form the foundation of the new physical chemistry.

Raoult's work is by no means limited to the study of the lowering of the freezing-point and of the vapor-tension of solvents. It should, however, be stated that probaby the most accurate cryoscopic measurements which have ever been made are those which were recently published by Raoult. His earlier work had to do with problems of a purely physical nature. Indeed, one of his earliest investigations threw much light on the action of the voltaic cell.

In thinking of Raoult we must not confine ourselves to the work which he has done, as brilliant as it is, but must remember the noble character and unassuming manner which were his characteristics. Abundant testimony to these attributes is furnished by all who knew Raoult, and the kind heart and singleness of purpose of his life are obvious to any one who has been favored with a line from his pen.

Raoult was born May 10, 1830, at Fournes (Nord), and was, therefore, nearly seventy-one years old when he died. The last thirty years of his life were spent at Grenoble in scientific investigation and in building up the institution with which he was connected. In 1889 he was elected dean of the faculty of sciences, a position which he held until his death.

He was loved by all who knew him and admired by all true men of science. H. C. J.

REPORTS.

The Action of Water upon Rocks.[1]

A recent number of this JOURNAL[2] contained a review of the work of Gautier upon the combustible gases present in the atmosphere and the probable source of the hydrogen existing there in a free condition. The results obtained led to an investigation of the probable origin of the gases which escape from the earth and their formation from the rocks. Reports of these researches show that the formation of the gases and the composition of many complex rocks can be explained readily without the assumption of any exterior agent. The escape of gases in mineral waters and from volcanoes and the cause, perhaps, of the violence of volcanic eruptions are explained and demonstrated by experiment. The author remarks

[1] Gautier: Compt. rend., 132, 58, 189, 518, 740, 932.

[2] This JOURNAL, 25, 344.

that it may appear rather paradoxical to expect to obtain any results by heating rocks which were originally formed from a fused mass and have been exposed to the action of heat for centuries, the intensity of the heat depending upon the depth of the rocks below the surface. A fact of great importance, and one which must be taken into consideration, is that the rocks were subjected to a pressure sufficient to prevent dissociation. If, however, conditions of pressure were changed, the possibility of reactions arose, and it was this problem which attracted the attention of the investigator.

When granite is heated to 100° with acid or to 300° with water alone a large volume of gas is formed. In two experiments, in each of which 1000 grams of granite, quarried from the same place at intervals of eight months, were heated in a vacuum to 100° with phosphoric acid and water, the following amounts of gas, calculated at 0° and 760 mm. pressure, were obtained :

	Volume of gas in cc. I.	II.
HCl, $SiFl_4$	trace	trace
H_2S	1.33	22.7
CO_2	272.6	237.5
Hydrocarbon absorbed by bromine	12.3	5.3
CH_4	trace	trace
H	53.05	191.48
N and argon	232.50	102.48
	571.78	559.46

Specimens heated with water alone to 300° gave the following results :

H_2S	1.3	1.0
CO_2	7.2	5.3
H	46.00	14.6
N	0.3	5.9

Soluble sulphides, which did not previously exist in the water, were found after the action was over and a comparison of the gas with that from volcanoes showed a strong resemblance.

The author shows that, in order to explain the action taking place in the earth, it is not necessary to assume, as is generally done, that surface water should penetrate to the seat of the action, as the rocks contain sufficient water to cause a very considerable decomposition. That this water is not present as water of constitution is shown from the fact that the rate and amount given off is not regular, but dependent

upon the temperature. The results obtained with four varieties of rocks, representing both acid and basic varieties, show that all varieties of rocks contain large amounts of water :

	Loss per 1000 grams of rock. 15°–250°.	250°–1000°.
Granite	2.29	7.35
Porphyry	5.80	12.40
Ophite	....	15.06
Lherzolite	....	16.80

The following results will give some idea of the amount of gas that can be formed and its relation to the volume of the rock :

Granite. Acid rock.	I.	II.	III.
Total vol. at 0° and 760 mm. pressure per 1000 grams of rock	2709 cc.	4209 cc.	2570 cc.
Composition per 100 volumes :			
CO_2	14.80	8.98	14.42
H_2S	trace	1.71	0.69
CO	4.93	5.12	5.50
CH_4	2.24	1.09	1.99
H	77.30	82.80	76.80
N and Ar	0.83	0.42	0.40
	100.10	100.12	99.80
Volume calculated for 1000 grams of rock :			
CO_2	400.6	378.0	370.6
H_2S	trace	71.9	18.7
CO	133.4	215.2	141.3
CH_4	60.6	45.8	51.1
H	2092.5	3481.0	1977.7
N	22.7	10.6	10.3
	2709.5	4209.5	2569.7

1000 grams or 376 cc. of granite, gave an average of 3162 cc. of gas, or 6.7 times its own volume. In a similar way another acid rock, porphyry, gave about 7.6 times the volume of the rock. Ophite, a basic rock, gave 7.6 times the volume of the rock, while lherzolite gave 15.7.

We see, therefore, that from 100 vols. of granite 670 vols. of gas were obtained ; from 100 vols. of porphyry 760 vols. of gas were obtained ; from 100 vols of ophite 760 vols. of gas

were obtained; while from 100 vols. of lherzolite 1570 vols. of gas were obtained.

The assumption that the gas is present as such in the rocks is no longer tenable, as some of these rocks have no cavities and the gas would have to be under a pressure sufficient to liquefy carbon dioxide.

If the gases were present as such in the rock they should be evolved at a constant rate when the rock is heated, but the following experiments show that this is not the case:

Granite.	First third.	Balance.
CO_2	20.19	6.13
H_2S	1.28	0.41
CO	0.57	1.02
CH_4	2.04	0.80
H	75.54	91.64
N	0.30	0.30
	99.92	100.30

A somewhat similar result was obtained when ophite was used.

As the action in the interior of the earth is causing constant weakening in some places and upheavals in others, there is abundant opportunity for fresh portions of rock to come under the influence of a greatly increased temperature and undergo changes similar to those which occur in the laboratory under similar conditions. There is no need to call to our aid any mysterious agent in order to explain volcanic explosions, as we find that the amount of gas formed, by the action of the enclosed water on the rock, is sufficient to explain the great explosive power. We can get a better idea of this, perhaps, when we consider that 1000 cc. of granite give, at 1000°, 20 liters of gas and 89 liters of water vapor.

As has already been pointed out, the hydrogen does not exist as such in the rock, but is formed by the action of the water on the rock. If many ferrous salts are heated to 750° or 800° with steam, hydrogen and an oxide of iron are formed, while ferrous sulphide yields a mixture of hydrogen and hydrogen sulphide, the proportion of the latter diminishing as the temperature increases. If siderite, the natural carbonate of iron, is heated with water, the following gases are formed: carbon dioxide, carbon monoxide, hydrogen sulphide, hydrogen and nitrogen. The nitrogen is formed from the nitride present as an impurity and the carbon monoxide is formed by the reduction of the carbon dioxide by the oxide of iron. As a similar reaction takes place when a silicate of iron is heated

with steam we can understand how mica, hornblende, pyroxene, biotite, etc., form hydrogen when they are heated with steam. If the hydrogen is confined and under pressure the reverse action takes place with the formation of ferrous salts, and this interchange continues until a state of equilibrium is reached when both ferrous and ferric silicates, such as are commonly found in the micas, pyroxenes, etc., are present. In an experiment carried out in the laboratory, 150 grams of ophite were heated to 250° to expel water and then to red heat, when 2.25 grams of water of constitution and 371 cc. of gas were formed. This residue was then cooled in a vacuum and heated with steam, when 70 cc. of gas were obtained. This gas could not have preexisted in it, but was formed by the action of the water.

The fact that, besides the gases already mentioned, hydrogen sulphide, marsh gas, and others are found in small quantity in the gases escaping from the earth requires explanation, and this subject has received attention. As already stated, the hydrogen is due to the decomposition of the iron compounds and silicates by water vapor, the carbon dioxide to dissociation of the carbonates and the carbon monoxide partly to reduction of carbon dioxide.

The author has devised a method for detecting free hydrogen sulphide, soluble sulphides, polysulphides, and hyposulphites in the same solution, and tests made with natural and artificial waters have led to the same conclusion as that reached by Henry, Boullay, and others, that the majority of sulphur waters contain the sulphur as an alkaline sulphide (nearly always sodium sulphide) with small amounts of sulphydrate, the proportion of the latter depending upon the amount of carbon dioxide present. The method used in this separation consists in distilling the water in a vacuum when the free hydrogen sulphide is driven out. If now carbon dioxide is passed through the solution, in which the temperature is kept below 30°, the soluble sulphide is decomposed with the formation of hydrogen sulphide, which is expelled as before. The sulphur in the form of hyposulphites is determined by titration with an iodine solution, and the sulphur of the polysulphides, after being liberated by acid, is oxidized by nitric acid and determined as barium sulphate.

Owing to the fact that sulphur waters escape from the earth from deposits that contain no soluble sulphur compounds, it has been difficult to explain their origin. The results obtained in this work, however, show that the formation can be readily explained on the basis of laboratory experiments. If powdered granite is treated for some time with cold water and the solu-

tion tested, it is found to be free from hydrogen sulphide and alkaline sulphides and contains chiefly silicate of soda and calcium sulphate. This test, as carried out, shows that no sulphides of the alkalies or alkaline earths are present in the granite. If, however, the granite is heated, in a sealed tube, with water to 250° to 300°, a true artificial sulphur water is formed which has the characteristic odor and alkaline reaction, and in which sodium sulphide, ammonium salts, phosphates, sulphates, and silicates, carbon dioxide, and nitrogen can be detected. As the test with cold water shows the absence of soluble sulphides and as the sulphide of iron does not react with water except at a high temperature and other metals, whose sulphides are decomposed by water, are not present, the formation of hydrogen sulphide cannot be ascribed to these substances. When an igneous rock is heated to redness, several gases, including hydrogen and carbon monoxide, are formed.

If now these gases are retained in cavities in the rocks and subjected to high pressure, they, along with carbon, in the presence of hydrogen sulphide, formed by the action of water on the sulphide of iron, act upon the feldspars, kaolins, etc., to form sulphosilicates and oxysulphides. These substances would be decomposed by hot water; but, under the action of pressure as the mass cooled, a condition of equilibrium would be reached when small amounts of the sulphur compounds would remain in the rocks. These substances, when heated with water, form soluble sulphides and hydrogen sulphide, and it is to these, present in small quantities in the rock, that the sulphur gases of mineral waters owe their origin.

If some albite is heated with water to 300° there is no trace of hydrogen sulphide formed; but if the material is placed in a tube, which also contains some granite, so arranged that the gases formed from the granite can react, under pressure, upon the albite, the latter, after this action, yields, when heated with water, hydrogen sulphide. This action is due to the formation of sulpho and oxysulpho compounds, some of which have been isolated in pure crystalline condition.

The ammonium salts which are so often found in mineral waters are formed, along with the nitrogen, by the action of water on the nitrides, which have been detected in the igneous rocks and in several cases isolated in a crystalline condition. Iodine and arsenic, which also commonly accompany sulphur compounds in mineral waters, have been detected by Gautier in the rocks from which the waters are charged with their solid and gaseous constituents.

We can thus explain the origin of all the gases occurring

in volcanic gases and in mineral waters by the action of water and heat on substances present in the igneous rocks, the hydrogen sulphide being formed by the action of water on the sulphosilicates and oxysulphide of carbon, the carbon dioxide by dissociation of carbonates, the carbon monoxide by reduction of the carbon dioxide, hydrogen by the action of water on ferrous silicates, hydrocarbons from the carbides, nitrogen and ammonium salts from the nitrides, and the sulphocyanates from the action of the ammonium salts and carbon dioxide.

These results, based on laboratory experiments, offer, therefore, a simple explanation of reactions which have hitherto been considered inexplicable. J. ELLIOTT GILPIN.

REVIEWS.

ENGINEERING CHEMISTRY: A Manual of Quantitative Chemical Analysis, for the Use of Students, Chemists, and Engineers. By THOMAS B. STILLMAN, M.Sc., PH.D., Professor of Analytical Chemistry in the Stevens Institute of Technology. Second edition. Easton, Pa.: The Chemical Publishing Co. 1900. pp. xxii + 503.

This second edition of Professor Stillman's book does not very greatly differ from the first, published in 1897. The number of pages is a little smaller, and there are not quite so many illustrations. The omission of a few subjects which had no proper place in a work on chemistry as applied to engineering is an improvement, a few useful additions have been made, and some changes in the order in which the various subject-matters are taken up have also been advantageous. But nothing has been introduced in regard to lime, lime mortar, stucco, or explosives, although these should certainly receive notice in a work on engineering chemistry. And, almost without exception, individual errors pointed out in a notice of the first edition remain uncorrected. J. W. M.

ANORGANISCHE FERMENTE. Darstellung kolloidaler Metalle auf elektrischem Wege, und Untersuchung ihrer katalytischen Eigenschaften. Kontaktchemische Studie von DR. PHIL. GEORG BREDIG, Privatdozent der Chemie a. d. Universität Leipzig. Mit 6 Figuren im Text. pp 99. Leipzig: Wilhelm Engelmann. 1901.

This monograph is an outgrowth of the important paper by Bredig and von Berneck on "Inorganic Ferments," which appeared in the Jubilee volume of the Zeitschrift für Physikalische Chemie, which was dedicated to van 't Hoff by his students. The original paper has been largely supplemented by an introductory chapter on methods of preparing colloidal solutions of the metals, and by subsequent experimental work with Ikeda and Reinders.

The general method employed in preparing colloidal solu-

tions of the metals consists in passing a suitable current between two bars of the metal immersed in pure water. In this way solutions of platinum, iridium, gold, palladium, silver, cadmium, etc., have been obtained.

The second part of the monograph deals with the properties of such solutions, and especially with their catalytic decomposition of hydrogen dioxide. The author sees in the contact action of these colloidal solutions of the metals an analogy to the action of organic ferments, whence the title of the monograph. A very small amount of platinum in solution in water can decompose a large amount of hydrogen dioxide. This action can be prevented by the presence of mere traces of certain substances like hydrogen sulphide, hydrocyanic acid, etc., a fact that suggests the action of very small quantities of certain poisons on organic ferments.

The work is extremely interesting, not only to the physical chemist but to the physiologist, and can be heartily recommended to all who have to deal in any way with the subject of fermentation. H. C. J.

CORRESPONDENCE.

Moscow, the 2/15 April, 1901.

TO THE EDITOR:

Sir: I beg you to accept my most sincere thanks for your friendly congratulations on the occasion of the celebration of my fortieth year of service.

Finding it quite impossible to address my heartfelt thanks directly to every one of all the American chemists who did me the honor to send me their congratulations, I beg that you will have the kindness to let me express to them the sentiments of my deepest gratitude in the pages of the AMERICAN CHEMICAL JOURNAL, by inserting there this letter.

Accept, sir, the expression of the most distinguished salutation of

Yours very truly,

PROF. DR. H. MARKOWNIKOFF.

CORRECTIONS.

Vol. 24, page 257, line 9: *After* "silver" *insert* "per cubic centimeter."

Vol. 24, page 258: The last equation should be

$$\overline{NO_3} + \overline{NO_2} + 2\overset{++}{Ag} + I_2 + H_2O = 2AgI + 2\overset{++}{H} + 2\overline{NO_3}.$$

Vol. 24, page 259, line 8: *For* "Danner" *read* "Dorrer."